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(54) Title: STYLING SHAMPOO COMPOSITIONS WHICH DELIVER IMPROVED HAIR CURL RETENTION AND HAIR FEEL (57) Abstract Disclosed are hair styling shampoo compositions which comprise from about 5 % to about 50 % by weight of a surfactant selected from the group consisting of anionic surfactants, zwitterionic or amphoteric surfactants, and combinations thereof; from about 0.1 % to about 10 % by weight of an organic or silicone-grafted hair styling polymer; and from about 40 % to about 94.9 % by weight of water; wherein the Hair Feel Index (HFI) is at least about 0.65 and the Curl Retention Value (CRV) is at least about 70. The composition provides improved styling performance and improved hair feel from a shampoo composition.		

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STYLING SHAMPOO COMPOSITIONS WHICH DELIVER IMPROVED HAIR CURL RETENTION AND HAIR FEEL

FIELD OF THE INVENTION

The present invention relates to hair styling shampoo compositions which provide improved styling performance and improved hair feel. More particularly, the present invention relates to styling shampoo compositions which contain a deterative surfactant component and a hair styling polymer. The compositions, once applied to hair, exhibit a Hair Feel Index (HFI) of at least 0.65 and a Curl Retention Value (CRV) of at least 70.

BACKGROUND OF THE INVENTION

Many hair shampoo compositions provide acceptable cleaning but provide little or no styling benefits, e.g. body, hold, stiffness. To realize such benefits, separate cleaning and styling products are often used.

Recently, hair shampoo compositions have been developed which can provide cleaning and styling performance from a single product. Many of these products contain styling polymers in a compatible shampoo base. Three different types of styling polymers are used to deliver styling performance: dispersible polymers, latex polymers, and hydrophobic styling polymers dispersed in a hydrophobic volatile carrier.

The first type of styling polymer is a polymer which can be dispersed in the aqueous shampoo matrix. This dispersible styling polymer may form a complex, or coacervate phase, with the deterative surfactant component in the shampoo or form a coacervate phase upon dilution. Upon dilution, the coacervate phase deposits on the hair. As the hair dries, the dispersible styling polymer entrapped in the coacervate delivers style achievement and style retention performance to the hair. Unfortunately, these dispersible styling polymers are very similar, if not identical, to the conditioning polymers used in 2-in-1 shampoo applications. As a result, when sufficient quantities are used to deliver styling performance, the resulting hair feel profile is unacceptable. The dispersible styling polymers have no inherent adhesive properties, consequently so much coacervate phase needs to be deposited on the hair to give styling performance that, after repeated usage, the hair is left overconditioned, coated, and dirty feeling.

The second type of styling polymer is a latex polymer. The latex polymer is in the form of a colloidal suspension of polymer particles in the aqueous shampoo matrix. In order to achieve adhesion between hair fibers, the glass transition temperature, or T_g , of the latex styling polymer must be significantly below room temperature. As a result, the latex styling polymers that give good styling performance have unacceptable hair feel which can be characterized as sticky and coated.

The third type of styling polymer is an adhesive, hydrophobic styling polymer. To prepare a styling shampoo with a hydrophobic styling polymer, the styling polymer is first dissolved in a volatile, water-insoluble carrier and then incorporated into the shampoo base. The water insoluble carrier thereafter

helps disperse the hydrophobic styling polymer in the shampoo composition, and also helps enhance spreading of the hydrophobic styling polymer onto hair such that the polymer sets and forms welds between hair fibers. The enhanced spreading of the styling polymer onto the hair results in improved styling performance from the shampoo composition.

One method for further improving styling polymer deposition from a shampoo, utilizing either type of styling polymer, involves the use of cationic deposition polymers. These cationic deposition polymers improve the deposition efficiency of the styling polymers, which in turn also improves styling performance. The improved deposition from the cationic polymer can also allow for reduction of the amount of styling polymer formulated into the shampoo composition, thus reducing raw material costs. The problem has been that excessive amounts of such deposition polymers can result in undesirably coated or oily wet hair feel, and can cause the hair when dry to feel dirty and have less body, less fullness.

Therefore, a need exists for styling shampoo compositions which provide good style achievement and style retention without the disadvantages of overconditioning, coated, or dirty feeling compositions. Surprisingly, the present invention provides hair styling shampoo compositions having good styling performance without being overconditioning, coated, or dirty feeling. The resulting hair styles obtained from using these compositions hold up well under the common stress conditions. Importantly, such compositions provide the benefit of allowing the user to achieve the desired style without separate style achievement products, such as mousses or gels, or to supplement their current style achievement products to more easily achieve the desired style. The styling compositions of the present invention leave the hair both feeling and looking natural. Also, these products do not have the disadvantage of causing the hair to quickly resoil.

It has been found in the present invention that compositions having certain properties, as defined by a Hair Feel Index (HFI) and a Curl Retention Value (CRV), are particularly useful for providing strong styling performance in combination with good hair feel. The hair styling compositions, when evaluated while the hair is still wet, exhibit a Hair Feel Index (HFI) of at least 0.65 and a Curl Retention Value (CRV) of at least 70. The compositions of the present invention provide the recited benefits by utilizing a hair styling polymer.

In view of the foregoing, it is therefore an object of this invention to provide styling shampoo compositions that provide good styling performance without unacceptable hair feel. It is a further object of this invention is to provide styling shampoo compositions containing a deterative surfactant component in combination with a styling polymer. It is another object of this invention to provide methods for evaluating styling performance and hair feel.

SUMMARY OF THE INVENTION

The present invention relates to styling shampoo compositions which comprise from about 5% to about 50% by weight of a surfactant selected from the group consisting of anionic surfactants, zwitterionic or amphoteric surfactants, and combinations thereof; from about 0.1% to about 10% by weight of a hair

styling polymer; and from about 40% to about 94.9% by weight of water, wherein the composition is characterized by providing a Hair Feel Index (HFI) of at least 0.65 and a Curl Retention Value (CRV) of at least 70.

DETAILED DESCRIPTION OF THE INVENTION

The shampoo compositions of the present invention can comprise, consist of, or consist essentially of the essential elements and limitations of the invention described herein, as well any of the additional or optional ingredients, components, or limitations described herein.

As used herein, the term "water-insoluble" refers to any material that has a solubility in water at 25°C of less than about 0.5%, preferably less than about 0.3%, even more preferably less than about 0.2% by weight.

As used herein, the symbol " \geq " means greater than or equal to.

All percentages, parts and ratios are based on the total weight of the shampoo compositions of the present invention, unless otherwise specified. All such weights as they pertain to listed ingredients are based on the active level and, therefore, do not include carriers or by-products that may be included in commercially available materials, unless otherwise specified.

The styling shampoo compositions of the present invention, including the essential and some optional components thereof, are described in detail hereinafter.

Detergent Surfactant Component

The styling shampoo compositions of the present invention comprise an detergent surfactant component to provide cleaning performance to the composition. The detergent surfactant component in turn comprises anionic detergent surfactant, zwitterionic or amphoteric detergent surfactant, or a combination thereof. Such surfactants should be physically and chemically compatible with the essential components described herein, or should not otherwise unduly impair product stability, aesthetics or performance.

Suitable anionic detergent surfactant components for use in the shampoo composition herein include those which are known for use in hair care or other personal care cleansing compositions. The concentration of the anionic surfactant component in the shampoo composition should be sufficient to provide the desired cleaning and lather performance, and generally range from about 0.5% to about 50%, preferably from about 5% to about 30%, more preferably from about 10% to about 25%, even more preferably from about 12% to about 22%, by weight of the composition.

Preferred anionic surfactants suitable for use in the shampoo compositions are the alkyl and alkyl ether sulfates. These materials have the respective formulae ROSO_3M and $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$, wherein R is alkyl or alkenyl of from about 8 to about 18 carbon atoms, x is an integer having a value of from 1 to 10, and M is a cation such as ammonium, alkanolamines, such as triethanolamine, monovalent metals, such as sodium and potassium, and polyvalent metal cations, such as magnesium, and calcium. Solubility of the surfactant will depend upon the particular anionic detergent surfactants and cations chosen.

Preferably, R has from about 8 to about 18 carbon atoms, more preferably from about 10 to about 16 carbon atoms, even more preferably from about 12 to about 14 carbon atoms, in both the alkyl and alkyl ether sulfates. The alkyl ether sulfates are typically made as condensation products of ethylene oxide and monohydric alcohols having from about 8 to about 24 carbon atoms. The alcohols can be synthetic or they can be derived from fats, e.g., coconut oil, palm kernel oil, tallow. Lauryl alcohol and straight chain alcohols derived from coconut oil or palm kernel oil are preferred. Such alcohols are reacted with between about 0 and about 10, preferably from about 2 to about 5, more preferably about 3, molar proportions of ethylene oxide, and the resulting mixture of molecular species having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

Specific non limiting examples of alkyl ether sulfates which may be used in the shampoo compositions of the present invention include sodium and ammonium salts of coconut alkyl triethylene glycol ether sulfate, tallow alkyl triethylene glycol ether sulfate, and tallow alkyl hexaoxyethylene sulfate. Highly preferred alkyl ether sulfates are those comprising a mixture of individual compounds, wherein the compounds in the mixture have an average alkyl chain length of from about 10 to about 16 carbon atoms and an average degree of ethoxylation of from about 1 to about 4 moles of ethylene oxide.

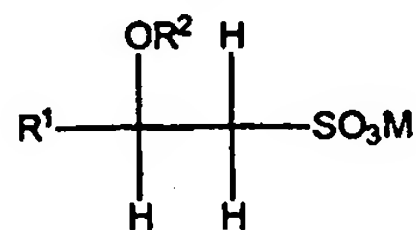
Other suitable anionic deterative surfactants are the water-soluble salts of organic, sulfuric acid reaction products conforming to the formula $[R^1-SO_3-M]$ where R^1 is a straight or branched chain, saturated, aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 10 to about 18, carbon atoms; and M is a cation described hereinbefore. Non limiting examples of such deterative surfactants are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, and n-paraffins, having from about 8 to about 24 carbon atoms, preferably about 12 to about 18 carbon atoms and a sulfonating agent, e.g., SO_3 , H_2SO_4 , obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated C_{10} to C_{18} n-paraffins.

Still other suitable anionic deterative surfactants are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil or palm kernel oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil or palm kernel oil. Other similar anionic surfactants are described in U.S. Patent 2,486,921; U.S. Patent 2,486,922; and U.S. Patent 2,396,278, which descriptions are incorporated herein by reference.

Other anionic deterative surfactants suitable for use in the shampoo compositions are the succinates, examples of which include disodium N-octadecylsulfosuccinate; disodium lauryl sulfosuccinate; diammonium lauryl sulfosuccinate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; and dioctyl esters of sodium sulfosuccinic acid.

Other suitable anionic deterative surfactants include olefin sulfonates having about 10 to about 24 carbon atoms. In this context, the term "olefin sulfonates" refers to compounds which can be produced by the sulfonation of alpha-olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sulfones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid SO₂, chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous SO₂, etc., when used in the gaseous form. The alpha-olefins from which the olefin sulfonates are derived are mono-olefins having from about 10 to about 24 carbon atoms, preferably from about 12 to about 16 carbon atoms. Preferably, they are straight chain olefins. In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process. A non limiting example of such an alpha-olefin sulfonate mixture is described in U.S. Patent 3,332,880, which description is incorporated herein by reference.

Another class of anionic deterative surfactants suitable for use in the shampoo compositions are the beta-alkyloxy alkane sulfonates. These surfactants conform to the formula



where R¹ is a straight chain alkyl group having from about 6 to about 20 carbon atoms, R² is a lower alkyl group having from about 1 to about 3 carbon atoms, preferably 1 carbon atom, and M is a water-soluble cation as described hereinbefore.

Preferred anionic deterative surfactants for use in the shampoo compositions include ammonium lauryl sulfate, ammonium laureth sulfate, triethylamine lauryl sulfate, triethylamine laureth sulfate, triethanolamine lauryl sulfate, triethanolamine laureth sulfate, monoethanolamine lauryl sulfate, monoethanolamine laureth sulfate, diethanolamine lauryl sulfate, diethanolamine laureth sulfate, lauric monoglyceride sodium sulfate, sodium lauryl sulfate, sodium laureth sulfate, potassium lauryl sulfate, potassium laureth sulfate, sodium lauryl sarcosinate, sodium lauroyl sarcosinate, lauryl sarcosine, cocoyl sarcosine, ammonium cocoyl sulfate, ammonium lauroyl sulfate, sodium cocoyl sulfate, sodium lauroyl sulfate, potassium cocoyl sulfate, potassium lauryl sulfate, triethanolamine lauryl sulfate, triethanolamine lauryl sulfate, monoethanolamine cocoyl sulfate, monoethanolamine lauryl sulfate, sodium tridecyl benzene sulfonate, sodium dodecyl benzene sulfonate, and combinations thereof.

Suitable amphoteric or zwitterionic deterative surfactants for use in the shampoo composition herein include those which are known for use in hair care or other personal care cleansing. Concentration of such amphoteric deterative surfactants preferably ranges from about 0.5 % to about 20%, preferably

from about 1% to about 10%, by weight of the composition. Non limiting examples of suitable zwitterionic or amphoteric surfactants are described in U.S. Patents 5,104,646 (Bolich Jr. et al.), U.S. Patent 5,106,609 (Bolich Jr. et al.), which descriptions are incorporated herein by reference.

Amphoteric deterative surfactants suitable for use in the shampoo composition are well known in the art, and include those surfactants broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group such as carboxy, sulfonate, sulfate, phosphate, or phosphonate. Preferred amphoteric deterative surfactants for use in the present invention include cocoamphoacetate, cocoamphodiacetate, lauroamphoacetate, lauroamphodiacetate, and mixtures thereof.

Zwitterionic deterative surfactants suitable for use in the shampoo composition are well known in the art, and include those surfactants broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic group such as carboxy, sulfonate, sulfate, phosphate or phosphonate. Zwitterionics such as betaines are preferred.

The shampoo compositions of the present invention may further comprise additional surfactants for use in combination with the anionic deterative surfactant component described hereinbefore. Suitable optional surfactants include nonionic surfactants. Any such surfactant known in the art for use in hair or personal care products may be used, provided that the optional additional surfactant is also chemically and physically compatible with the essential components of the shampoo composition, or does not otherwise unduly impair product performance, aesthetics or stability. The concentration of the optional additional surfactants in the shampoo composition may vary with the cleansing or lather performance desired, the optional surfactant selected, the desired product concentration, the presence of other components in the composition, and other factors well known in the art.

Non limiting examples of other anionic, zwitterionic, amphoteric or optional additional surfactants suitable for use in the shampoo compositions are described in McCutcheon's, Emulsifiers and Detergents, 1989 Annual, published by M. C. Publishing Co., and U.S. Patent 3,929,678, U.S. Patent 2,658,072; U.S. Patent 2,438,091; U.S. Patent 2,528,378, which descriptions are incorporated herein by reference.

Styling polymer

The shampoo compositions of the present invention comprise a hair styling polymer, concentrations of which range from about 0.1% to about 10%, preferably from about 0.3% to about 7%, more preferably from about 0.5% to about 5%, by weight of the composition. These styling polymers provide the shampoo composition of the present invention with hair styling performance by providing polymeric deposits on the hair after application from a shampoo composition.

Many such polymers are known in the art, including dispersible and water-insoluble organic polymers and water-insoluble silicone-grafted polymers, all of which are suitable for use in the shampoo composition herein provided that they also have the requisite features or characteristics described hereinafter. Such polymers can be made by conventional or otherwise known polymerization techniques well known in the art, an example of which includes free radical polymerization.

Examples of suitable organic and silicone grafted polymers for use in the shampoo composition of the present invention are described in greater detail hereinafter. Examples of dispersible polymers are disclosed in, for example, U.S. Patent 5,391,368, which descriptions are incorporated by reference herein. Examples of latex polymers are disclosed in, for example, U.S. Patent 4,710,374, which descriptions are incorporated by reference herein.

I. Organic styling polymer

The hair styling polymers suitable for use in the shampoo composition of the present invention include organic hair styling polymers well known in the art. The organic styling polymers may be homopolymers, copolymers, terpolymers or other higher polymers, but must comprise one or more polymerizable hydrophobic monomers to thus render the resulting styling polymer hydrophobic and water-insoluble as defined herein. The styling polymers may therefore further comprise other water soluble, hydrophilic monomers provided that the resulting styling polymers have the requisite hydrophobicity and water insolubility.

As used herein, the term "hydrophobic monomer" refers to polymerizable organic monomers that can form with like monomers a water-insoluble homopolymer, and the term "hydrophilic monomer" refers to polymerizable organic monomers that can form with like monomers a water-soluble homopolymer.

The organic styling polymers preferably have a weight average molecular weight of at least about 20,000, preferably greater than about 25,000, more preferably greater than about 30,000, most preferably greater than about 35,000. There is no upper limit for molecular weight except that which limits applicability of the invention for practical reasons, such as processing, aesthetic characteristics, formulateability, etc. In general, the weight average molecular weight will be less than about 10,000,000, more generally less than about 5,000,000, and typically less than about 2,000,000. Preferably, the weight average molecular weight will be between about 20,000 and about 2,000,000, more preferably between about 30,000 and about 1,000,000, and most preferably between about 40,000 and about 500,000.

The organic styling polymers also preferably have a glass transition temperature (T_g) or crystalline melting point (T_m) of at least about -20°C , preferably from about 20°C to about 80°C , more preferably from about 20°C to about 60°C . Styling polymers having these T_g or T_m values form styling films on hair that are not unduly sticky or tacky to the touch. As used herein, the abbreviation " T_g " refers to the glass transition temperature of the backbone of the polymer, and the abbreviation " T_m " refers to the

crystalline melting point of the backbone, if such a transition exists for a given polymer. Preferably, both the T_g and the T_m, if any, are within the ranges recited hereinabove.

The organic styling polymers are carbon chains derived from polymerization of hydrophobic monomers such as ethylenically unsaturated monomers, cellulosic chains or other carbohydrate-derived polymeric chains. The backbone may comprise ether groups, ester groups, amide groups, urethanes, combinations thereof, and the like.

The organic styling polymers may further comprise one or more hydrophilic monomers in combination with the hydrophobic monomers described herein, provided that the resulting styling polymer has the requisite hydrophobic character and water-insolubility. Suitable hydrophilic monomers include, but are not limited to, acrylic acid, methacrylic acid, N,N-dimethylacrylamide, dimethyl aminoethyl methacrylate, quaternized dimethylaminoethyl methacrylate, methacrylamide, N-t-butyl acrylamide, maleic acid, maleic anhydride and its half esters, crotonic acid, itaconic acid, acrylamide, acrylate alcohols, hydroxyethyl methacrylate, diallyldimethyl ammonium chloride, vinyl ethers (such as methyl vinyl ether), maleimides, vinyl pyridine, vinyl imidazole, other polar vinyl heterocyclics, styrene sulfonate, allyl alcohol, vinyl alcohol (such as that produced by the hydrolysis of vinyl acetate after polymerization), salts of any acids and amines listed above, and mixtures thereof. Preferred hydrophilic monomers include acrylic acid, N,N-dimethyl acrylamide, dimethylaminoethyl methacrylate, quaternized dimethyl aminoethyl methacrylate, vinyl pyrrolidone, salts of acids and amines listed above, and combinations thereof.

Suitable hydrophobic monomers for use in the organic styling polymer include, but are not limited to, acrylic or methacrylic acid esters of C₁-C₁₈ alcohols, such as methanol, ethanol, methoxy ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, t-butanol(2-methyl-2-propanol), cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-tri methyl-1-hexanol, 1-decanol, 1-dodecanol, 1-hexadecanol, 1-octa decanol, and the like, the alcohols having from about 1 to about 18 carbon atoms, preferably from about 1 to about 12 carbon atoms; styrene; polystyrene macromer; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; alpha-methylstyrene; t-butylstyrene; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene; and mixtures thereof. Preferred hydrophobic monomers include n-butyl methacrylate, isobutyl methacrylate, t-butyl acrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, vinyl acetate, and mixtures thereof, more preferably t-butyl acrylate, t-butyl methacrylate, or combinations thereof. Surprisingly, it has been found that conventional styling polymers consisting of copolymers of vinyl pyrrolidone and vinyl acetate do not exhibit the curl retention benefits required of the present invention.

The styling polymers for use in the shampoo composition preferably comprise from about 20% to 100%, more preferably from about 50% to about 100%, even more preferably from about 60% to about

100%, by weight of the hydrophobic monomers, and may further comprise from zero to about 80% by weight of hydrophilic monomers. The particular selection and combination of monomers for incorporation into the styling polymer will help determine its formulational properties. By appropriate selection and combination of, for example, hydrophilic and hydrophobic monomers, the styling polymer can be optimized for physical and chemical compatibility with the selected styling polymer solvent described hereinafter and other components of the shampoo composition. The selected monomer composition of the organic styling polymer must, however, render the styling polymer water-insoluble but soluble in the selected styling polymer solvent described hereinafter. In this context, the organic styling polymer is soluble in the styling polymer solvent if the organic polymer is solubilized in the solvent at 25° C at the polymer and solvent concentrations of the shampoo formulation selected. However, a solution of the organic styling polymer and styling polymer solvent may be heated to speed up solubility of the styling polymer in the styling polymer solvent. Such styling polymer and solvent formulation, including the selection of monomers for use in the styling polymer, to achieve the desired solubility is well within the skill of one in the art.

Examples of preferred organic styling polymers include *t*-butyl acrylate/2-ethylhexyl acrylate copolymers having a weight/weight ratio of monomers of about 95/5, about 90/10, about 80/20, about 70/30, about 60/40, and about 50/50; *t*-butyl acrylate/2-ethylhexyl methacrylate copolymers having a weight/weight ratio of monomers of about 95/5, about 90/10, about 80/20, about 70/30, about 60/40, and about 50/50; *t*-butyl methacrylate/2-ethylhexyl acrylate copolymers having a weight/weight ratio of monomers of about 95/5, about 90/10, about 80/20, about 70/30, about 60/40, and about 50/50; *t*-butyl methacrylate/2-ethylhexyl methacrylate copolymers having a weight/weight ratio of monomers of about 95/5, about 90/10, about 80/20, about 70/30, about 60/40, and about 50/50; *t*-butyl ethacrylate/2-ethylhexyl methacrylate copolymers having a weight/weight ratio of monomers of about 95/5, about 90/10, about 80/20, about 70/30, about 60/40, and mixtures thereof.

Especially preferred polymers are *t*-butyl acrylate/2-ethylhexyl methacrylate copolymers having a weight/weight ratio of monomers of about 95/5, about 90/10, about 80/20, about 70/30, about 60/40, and about 50/50; *t*-butyl methacrylate/2-ethylhexyl methacrylate copolymers having a weight/weight ratio of monomers of about 95/5, about 90/10, about 80/20, about 70/30, about 60/40, and about 50/50; and mixtures thereof.

Examples of other suitable styling polymers are described in U.S. Patent 4,272,511, to Papantoniou et al., issued June 9, 1981; U.S. Patent 5,672,576, to Behrens et al., issued September 30, 1997; and U.S. Patent 4,196,190, to Gehman et al., issued April 1, 1980, which descriptions are incorporated herein by reference.

II. Silicone-grafted styling polymer

Other suitable styling polymers for use in the shampoo composition of the present invention are silicone-grafted hair styling resins. These polymers may be used alone or in combination with the organic

styling polymers described hereinbefore. Many such polymers suitable for use in the shampoo composition herein are known in the art. These polymers are characterized by polysiloxane moieties covalently bonded to and pendant from an uncross-linked polymeric carbon-based backbone.

The backbone of the silicone-grafted polymer is preferably a carbon chain derived from polymerization of ethylenically unsaturated monomers, but can also be cellulosic chains or other carbohydrate-derived polymeric chains to which polysiloxane moieties are pendant. The backbone can also include ether groups, ester groups, amide groups, urethane groups and the like. The polysiloxane moieties can be substituted on the polymer or can be made by co-polymerization of polysiloxane-containing polymerizable monomers (e.g. ethylenically unsaturated monomers, ethers, and/or epoxides) with non-polysiloxane-containing polymerizable monomers. The silicone-grafted styling polymers preferably have a weight average molecular weight of at least about 10,000, preferably greater than about 20,000, more preferably greater than about 35,000, most preferably greater than about 50,000. The weight average molecular weight of the silicone-grafted styling polymer is preferably less than 300,000, more preferably less than about 250,000, and most preferably less than about 150,000.

The silicone-grafted styling polymers for use in the shampoo composition comprise "silicone-containing" (or "polysiloxane-containing") monomers, which form the silicone macromer pendant from the backbone, and non-silicone-containing monomers, which form the organic backbone of the polymer.

Preferred silicone-grafted polymers comprise an organic backbone, preferably a carbon backbone derived from ethylenically unsaturated monomers, such as a vinyl polymeric backbone, and a polysiloxane macromer (especially preferred are polydialkylsiloxane, most preferably polydimethylsiloxane) grafted to the backbone. As used hereinafter, the term "PDMS" refers to polydimethylsiloxane. The polysiloxane macromer should have a weight average molecular weight of at least about 500, preferably from about 1,000 to about 100,000, more preferably from about 2,000 to about 50,000, most preferably about 5,000 to about 20,000. Organic backbones contemplated include those that are derived from polymerizable, ethylenically unsaturated monomers, including vinyl monomers, and other condensation monomers (e.g., those that polymerize to form polyamides and polyesters), ring-opening monomers (e.g., ethyl oxazoline and caprolactone), etc. Also contemplated are backbones based on cellulosic chains, ether-containing backbones, etc.

Preferred silicone grafted polymers for use in the shampoo composition comprise monomer units derived from: at least one free radically polymerizable ethylenically unsaturated monomer or monomers and at least one free radically polymerizable polysiloxane-containing ethylenically unsaturated monomer or monomers.

The silicone grafted polymers suitable for use in the shampoo composition generally comprise from about 1% to about 50%, by weight, of polysiloxane-containing monomer units and from about 50% to about 99% by weight, of non-polysiloxane-containing monomers. The non-polysiloxane-containing

monomer units can be derived from the hydrophilic and/or hydrophobic monomer units described hereinbefore.

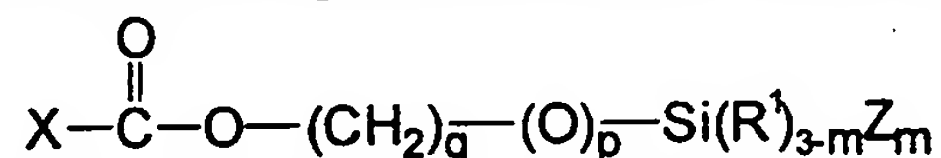
The styling polymer for use in the shampoo composition can therefore comprise combinations of the hydrophobic and/or polysiloxane-containing monomer units described herein, with or without hydrophilic comonomers as described herein, provided that the resulting styling polymer has the requisite characteristics as described herein.

Suitable polymerizable polysiloxane-containing monomers include, but are not limited to, those monomers that conform to the formula:

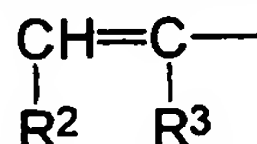


wherein X is an ethylenically unsaturated group copolymerizable with the hydrophobic monomers described herein, such as a vinyl group; Y is a divalent linking group; R is a hydrogen, hydroxyl, lower alkyl (e.g. C₁-C₄), aryl, alkaryl, alkoxy, or alkylamino; Z is a monovalent siloxane polymeric moiety having a number average molecular weight of at least about 500, which is essentially unreactive under copolymerization conditions, and is pendant from the vinyl polymeric backbone described above; n is 0 or 1; and m is an integer from 1 to 3. These polymerizable polysiloxane-containing monomers have a weight average molecular weight as described above.

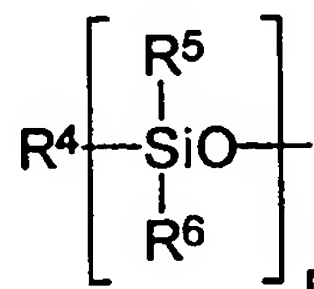
A preferred polysiloxane-containing monomer conforms to the formula:



wherein m is 1, 2 or 3 (preferably m = 1); p is 0 or 1; q is an integer from 2 to 6; R¹ is hydrogen, hydroxyl, lower alkyl, alkoxy, alkylamino, aryl, or alkaryl (preferably R¹ is alkyl); X conforms to the formula

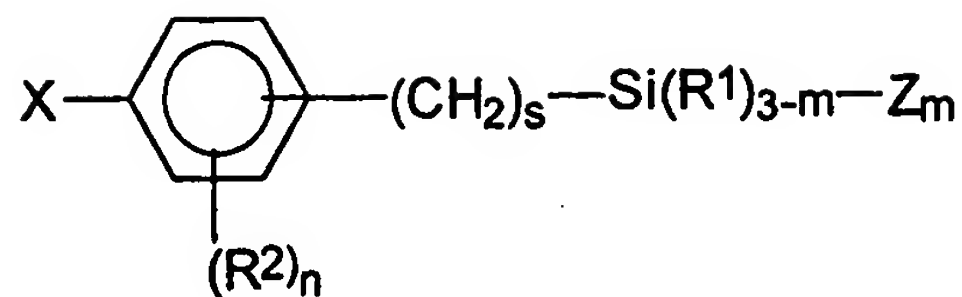


wherein R² is hydrogen or -COOH (preferably R² is hydrogen); R³ is hydrogen, methyl or -CH₂COOH (preferably R³ is methyl); Z conforms to the formula:

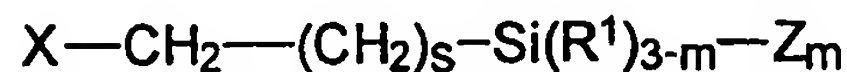


wherein R⁴, R⁵, and R⁶ independently are lower alkyl, alkoxy, alkylamino, aryl, arylalkyl, hydrogen or hydroxyl (preferably R⁴, R⁵, and R⁶ are alkyls); and r is an integer of about 5 or higher, preferably about 10 to about 1500 (most preferably r is from about 100 to about 250). Most preferably, R⁴, R⁵, and R⁶ are methyl, p=0, and q=3.

Another preferred polysiloxane monomer conforms to either of the following formulas



or



wherein: *s* is an integer from 0 to about 6, preferably 0, 1, or 2, more preferably 0 or 1; *m* is an integer from 1 to 3, preferably 1; *R*² is C1-C10 alkyl or C7-C10 alkylaryl, preferably C1-C6 alkyl or C7-C10 alkylaryl, more preferably C1-C2 alkyl; *n* is an integer from 0 to 4, preferably 0 or 1, more preferably 0.

The silicone grafted styling polymers suitable for use in the shampoo composition preferably comprise from about 50% to about 99%, more preferably from about 60% to about 98%, most preferably from about 75% to about 95%, by weight of the polymer, of non-silicone macromer-containing monomer units, e.g. the total hydrophobic and hydrophilic monomer units described herein, and from about 1% to about 50%, preferably from about 2% to about 40%, more preferably from about 5% to about 25%, of silicone macromer-containing monomer units, e.g. the polysiloxane-containing monomer units described herein. The level of hydrophilic monomer units can be from about 0% to about 70%, preferably from about 0% to about 50%, more preferably from about 0% to about 30%, most preferably from about 0% to about 15%; the level of hydrophobic monomer units, can be from 30% to about 99%, preferably from about 50% to about 98%, more preferably from about 70% to about 95%, most preferably from about 85% to about 95%.

Examples of some suitable silicone grafted polymers for use in the shampoo composition herein are listed below. Each listed polymer is followed by its monomer composition as weight part of monomer used in the synthesis:

- (i) t-butylacrylate/t-butyl-methacrylate/2-ethylhexyl-methacrylate/PDMS macromer-20,000 molecular weight macromer 31/27/32/10
- (ii) t-butylmethacrylate/2-ethylhexyl-methacrylate/PDMS macromer-15,000 molecular weight macromer 75/10/15
- (iii) t-butylmethacrylate/2-ethylhexyl-acrylate/PDMS macromer-10,000 molecular weight macromer 65/15/20
- (iv) t-butylacrylate/2-ethylhexyl-acrylate/PDMS macromer-14,000 molecular weight macromer 77/11/12
- (v) t-butylacrylate/2-ethylhexyl-methacrylate/PDMS macromer-13,000 molecular weight macromer 81/9/10

Examples of other suitable silicone grafted polymers for use in the shampoo composition of the present invention are described in EPO Application 90307528.1, published as EPO Application 0 408 311

A2 on January 11, 1991, Hayama, et al.; U.S. Patent 5,061,481, issued October 29, 1991, Suzuki et al.; U.S. Patent 5,106,609, Bolich et al., issued April 21, 1992; U.S. Patent 5,100,658, Bolich et al., issued March 31, 1992; U.S. Patent 5,100,657, Ansher-Jackson, et al., issued March 31, 1992; U.S. Patent 5,104,646, Bolich et al., issued April 14, 1992; U.S. Serial No. 07/758,319, Bolich et al, filed August 27, 1991, U.S. Serial No. 07/758,320, Torgerson et al., filed August 27, 1991, which descriptions are incorporated herein by reference.

Properties of Styling Shampoo Compositions

The styling shampoo compositions of the present invention exhibit specific physical properties as defined by the Hair Feel Index (HFI) and Curl Retention Index (CRV) which are determined as described below.

Compositions of the invention are characterized by having an HFI of at least 0.65 and a CRV of at least 70. Preferred compositions are characterized by having an HFI of at least 0.70 and a CRV of at least 75. More preferred compositions are characterized by having an HFI of at least 0.80 and a CRV of at least 80.

Methodology for Determining HFI and CRV:

The following applies in determining each value. The hair switches are made by Advanced Testing Laboratories (Cincinnati, OH). Also, the silicone containing non-styling shampoo has the following formulation:

Component	Weight %
Ammonium Laureth-3 Sulfate	15.0
Ammonium Lauryl Sulfate	5.0
Glycol Distearate	2.0
Dimethicone	1.5
Fragrance	0.7
Tricetyl Methylmonium Chloride	0.5
Cocamide MEA	0.85
Cetyl Alcohol	0.21
Stearyl Alcohol	0.09
Preservatives	0.3
Monosodium Phosphate	0.1
Disodium Phosphate	0.2
Water	73.55

The silicone containing non-styling shampoo is prepared in the following manner. A premix is prepared by solubilizing the solids in half of the ammonium laureth-3 sulfate and enough water such that the premix is 50% of the finished batch. The target premix temperature is 74°C. Next the premix is cooled to approximately 38°C. The dimethicone is emulsified as a separate premix using a portion of the ammonium laureth-3 sulfate. The dimethicone emulsion and the remaining components are then added to the batch with sufficient agitation to ensure a homogeneous composition.

Additionally, all water is 38°C tap water with a grain of 7 to 11 and a flow rate of 5.7 liters per minute. Also, care is taken to avoid contamination of a given product with another (e.g., by wearing clean gloves).

a) Hair Feel Index:

The Hair Feel Index (HFI) of a treated hair switch is determined by having panelists evaluate treated hair switches for two attributes, resistance and roughness, each on a scale of 0 to 10. For resistance, 0 is "no resistance" and 10 is "lots of resistance." For roughness, 0 is "not rough" and 10 is "extremely rough." The silicone containing non-styling shampoo is identified as the internal control for each attribute with an assigned value: 5.75 for resistance and 4.50 for roughness.

The hair switches used in the procedure are 2 gm/15.25 cm long, flat, and slightly bleached virgin brown hair from DeMeo Brothers in New York. Each switch is approximately 3.8 cm wide and is secured with a 2.5 cm high Plexiglas top.

In preparation for test product application, the switches are clipped together in pairs and then wetted with tap water. 2 cc of test product is applied to each pair of switches and is massaged, or milked, therein for 30 seconds such that the shampoo is distributed evenly throughout the switch. Each pair of switches is then rinsed with water for 30 seconds. The switch pair is then turned around and another 2 cc of test product is applied to each pair of switches and is massaged, or milked, therein for 30 seconds, followed by another 30 second rinse. This process of two treatments and two rinses is defined as a cycle. The switch pair is then unclipped, each individual switch is turned around so that the sides facing each other are now on the outside of the switch pair. The switch pair is then reclipped and a second cycle is applied. During the last two seconds of the second lather of this cycle, the switch pair is combed through once with a beautician's comb. The switch pair is then turned around and a third cycle is applied. The switch pair is then unclipped, quickly rinsed, and then combed through once. After rinsing, the excess water is squeezed from each switch by running the index and middle fingers along the length of the switch with firm pressure. The switches are placed on a foil covered tray and then covered with foil to keep them wet until the panelist is ready to evaluate them.

In preparation for control shampoo application, the switch pairs receive one cycle as defined above. The switch pair is then unclipped, quickly rinsed, and then combed through once. After rinsing, the excess water is squeezed from each switch by running the index and middle fingers along the length of the switch with firm pressure. The switches are placed on a foil covered tray and then covered with foil to keep them wet until the panelist is ready to evaluate them. A total of 24 switches are treated for each test product and the control.

Each panelist receives a tray with a control switch (identified) and two to three test products. The test products are randomized to avoid any bias associated with order. The panelists cleanse their fingertips with isopropyl alcohol swabs and allow them to dry prior to performing the evaluation. The control switch is dipped into a beaker of warm water, the excess water is squeezed from each switch by running the index

and middle fingers along the length of the switch with moderate pressure, and clipped to a horizontal bar. The same procedure is then followed for each test product. Once the switches are all hung on the bar, the panelists begin their evaluation. For each attribute, the control is evaluated first to establish a reference point for the panelist. The score for the control is pre-recorded on the test ballot.

First, the switches are evaluated for resistance. Slowly moving the index finger and middle finger along the switch, from top to bottom, the panelist feels for the presence or absence of drag when moving fingers down the hair switch. Each panelist records the resistance score. Next, the switches are evaluated for roughness. Slowly running the thumb and index finger along the switch, from top to bottom, the panelist feels for unevenness of the hair tress which would be associated with brittle or straw-like hair. Each panelist records the roughness score.

A minimum of twelve panelists evaluate the test product switches. The mean resistance is determined by averaging the resistance scores from each panelist for each test product. The mean roughness is determined by averaging the roughness scores from each panelist for each test product. The Resistance Index (ReI) is defined as the mean resistance score for each test product indexed to the control using the assigned resistance score for the control (5.75). The Roughness Index (RoI) is defined as the mean roughness score for each test product indexed to the control using the assigned roughness score for the control (4.50). The Hair Feel Index (HFI) is then defined by the following equation:

$$HFI = (ReI + RoI)/2.$$

b) Curl Retention Value:

The Curl Retention Value (CRV) is predictive of perceived style/hold benefits in styling shampoos by measuring the amount of curl retention over time.

This procedure utilizes curly permed hair switches which are prepared in the following manner. First, 4 gm/20.3 cm long, round switches are rinsed with water for 30 seconds and the excess water is squeezed from the switch using the first two fingers. Next, 0.5 cc of Perfect Comb Out waving lotion (ZOTOS) is applied to the bottom 5 cm of each switch using a syringe. Each switch is then divided into 3 equal sections. Once an end wrap is placed on the end of each section, each section is then curled by starting at the right side of a 0.95 cm diameter straight rod, wrapping the hair tightly and spirally along the length of the rod. Using a syringe, 8 cc of waving lotion is applied such that the entire switch is covered. The rolled switches are then placed in plastic bag or wrapped in cellophane 2 at a time. After 30 minutes, the switches are unrolled and checked to see if the desired wave pattern has been achieved. If not, the switches are then re-rolled and spot checked every 2 minutes until the desired wave pattern is achieved, being careful not to exceed a total of 45 minutes. With the rods still intact, the switches are then rinsed for 90 seconds and blotted with a paper towel to remove excess water. After blot drying, 10 cc of 20 volume peroxide is applied to each rolled switch. Five minutes later the rods are removed from the switches. The switches are rinsed with water for 1 minute, and blotted with a paper towel. Without combing, the switches are then laid flat on a Plexiglas tray and left to dry in a room at ambient temperature and relative

humidity. After 2 days, the switches are shampooed with Prell shampoo by applying 4 cc of Prell shampoo, lathering with for 30 seconds, rinsing with water for 30 seconds, applying another 4 cc of Prell shampoo, lathering for 30 more seconds, and rinsing with water again for 60 seconds. Each switch is blotted three times with a paper towel.

Next, the various products and control compositions are applied to the switches. For shampoo, 0.2 cc of shampoo is applied to each switch. The switch is lathered for 30 seconds and then rinsed for 30 seconds. A second 0.2 cc of shampoo is applied and the process is repeated, 30 seconds of lathering followed by 30 seconds of rinsing. During the lathering, the end of each switch is brought up to the top of the switch and scrubbed, hair against hair, to generate lather during the first 10 seconds. The switch is milked for the remaining 20 seconds. Upon completion of product application, each switch is combed through once with a small tooth beautician's comb and the excess water is squeezed from each switch by running the thumb and forefinger along the length of each switch such that the hair resembles a smooth, flat ribbon. Four switches are treated per test product and control.

Next, the hair of each switch is curled using a 22 mm diameter, 70 mm long 'magnetic' roller with a matching cover. The hair of each switch is curled by starting at the right side of the roller and wrapping the hair tightly around the roller, catching the hair ends under the hair strand as the hair is rolled with tension spirally up the roller. It is important to use the same amount of tension when curling all switch samples in order to ensure like test conditions. Once each switch is rolled, each roller is placed on end on a Plexiglas tray in a convection air drying box for 3 hours at approximately 57°C to 60°C and at an ambient relative humidity. Once drying is complete, the still-rolled switches are placed in a 27°C/15% relative humidity room and allowed to cool for about 30 minutes before the rollers are removed from the switches.

After cooling, the rollers are removed by carefully unrolling each switch. In preparation for curl fall measurements, each curled switch is hung vertically and grouped according to test product. The initial length of the curled switch (L_0) is measured from the lowest end of the clip holding the switch to the end of the switch. This measurement is taken to the nearest mm using a metric ruler. The switches are then placed in a 27°C /80% relative humidity room and the curl lengths are remeasured at 30 minutes (L_{30}) to determine the curl fall. The Curl Retention Value (CRV) for a switch is calculated using the following formula:

$$CRV = \frac{L - L_{30}}{L - L_0} \times 100\%$$

where L is the original length of the untreated switch; L_{30} is the length of the test product or control curl switch after 30 minutes; and L_0 is the length of the test product or control switch at the time of roller removal.

Optional Components

The shampoo compositions of the present invention may further comprise one or more optional components known for use in hair care or personal care products, provided that the optional components are physically and chemically compatible with the essential components described herein, or do not otherwise unduly impair product stability, aesthetics or performance. Individual concentrations of such optional components may range from about 0.001% to about 10% by weight of the shampoo compositions.

Non limiting examples of optional components for use in the shampoo composition include anti dandruff agents, conditioning agents (hydrocarbon oils, fatty esters, silicones) dyes, nonvolatile solvents or diluents (water soluble and insoluble), pearlescent aids, foam boosters, additional surfactants or nonionic cosurfactants, pediculocides, pH adjusting agents, perfumes, preservatives, proteins, skin active agents, sunscreens, vitamins, and viscosity adjusting agents.

The shampoo composition of the present invention preferably further comprises a water insoluble, volatile carrier for the hydrophobic styling polymer. The carrier helps disperse the styling polymer in the shampoo composition, and also helps enhance spreading of the styling polymer onto hair such that the polymer sets and forms a thin film onto the surface of the hair shaft. The optional a water insoluble, volatile carrier for the hydrophobic styling polymer is described in more detail hereinafter.

The shampoo composition of the present invention preferably further comprises select cationic deposition polymers to improve the deposition efficiency of the styling polymers, which in turn also improves styling performance. These optional cationic deposition polymers are described in more detail hereinafter.

The shampoo composition of the present invention preferably further comprises a select stability active to enhance the deposition efficiency of the hair styling polymer over conventional stabilizers, allowing for more formulation freedom to either lower the cationic deposition polymer usage level, or to incorporate new cationic deposition polymers with improved build-up profiles. These optional select stability actives are described in more detail hereinafter.

The shampoo composition of the present invention preferably further comprises select cationic materials which act as spreading agents for the styling polymer/volatile carrier droplets. These optional cationic spreading agents are described in more detail hereinafter.

The shampoo composition of the present invention also preferably comprises select polyalkylene glycols to enhance hair feel and enhance styling performance. These optional polyalkylene glycols are described in more detail hereinafter.

The shampoo composition of the present invention also preferably comprises a silicone hair conditioning agent to enhance hair feel, especially the soft, silky feel of dry hair. These optional silicone hair conditioning agents are described in more detail hereinafter.

The shampoo composition of the present invention also preferably comprises additional optional agents which improve the performance and/or aesthetics of the composition. These materials impact

which shampoo components are solubilized by the surfactant component and how much of each component is solubilized, influencing coacervate formation and composition. These additional agents are also entrapped in the coacervate, thus impacting styling performance and hair feel both directly and indirectly. These additional optional agents are described in more detail hereinafter.

a) Volatile Carrier for the Styling Polymer

The shampoo composition of the present invention may further comprise a volatile carrier for solubilizing the hair styling polymers described hereinbefore. The carrier helps disperse the hair styling polymer as water-insoluble fluid particles throughout the shampoo composition, wherein the dispersed particles comprise the styling polymer and the volatile carrier. Carriers suitable for this purpose include hydrocarbons, ethers, esters, amines, alkyl alcohols, volatile silicone derivatives and combinations thereof, many examples of which are well known in the art.

The volatile carrier must be water-insoluble or have a low water solubility. The selected styling polymer, however, must also be sufficiently soluble in the selected carrier to allow dispersion of the hair styling polymer and solvent combination as a separate, dispersed fluid phase in the shampoo composition.

The carrier for use in the shampoo composition must also be a volatile material. In this context, the term volatile means that the carrier has a boiling point of less than about 300°C, preferably from about 90°C to about 260°C, more preferably from about 100°C to about 200°C (at about one atmosphere of pressure).

The concentration of the volatile carrier in the shampoo composition must be sufficient to solubilize the hair styling polymer and disperse it as a separate fluid phase in the shampoo composition. Such concentrations generally range from about 0.10% to about 10%, preferably from about 0.5% to about 8%, most preferably from about 1% to about 6%, by weight of the shampoo composition, wherein the weight ratio of styling polymer to carrier is preferably from about 10:90 to about 70:30, more preferably from about 20:80 to about 65:35, even more preferably from about 30:70 to about 60:40. If the weight ratio of styling polymer to carrier is too low, the lathering performance of the shampoo composition is negatively affected. If the ratio of polymer to solvent is too high, the composition becomes too viscous and causes difficulty in the dispersion of the styling polymer. The hair styling agents should have an average particle diameter in the final shampoo product of from about 0.05 to about 100 microns, preferably from about 1 to about 25 microns, more preferably from about 0.5 to about 10 microns. Particle size can be measured according to methods known in the art, including, for example optical microscopy.

Preferred volatile carriers for use in the shampoo composition are the hydrocarbon solvents, especially branched chain hydrocarbon solvents. The hydrocarbon solvents may be linear or branched, saturated or unsaturated, hydrocarbons having from about 8 to about 18 carbon atoms, preferably from about 10 to about 16 carbon atoms. Saturated hydrocarbons are preferred, as are branched hydrocarbons. Nonlimiting examples of some suitable linear hydrocarbons include decane, dodecane, decene, tridecene, and combinations thereof. Suitable branched hydrocarbons include isoparaffins, examples of which

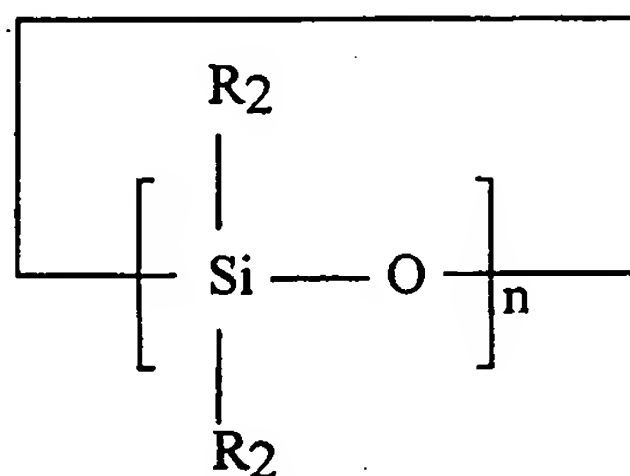
include commercially available isoparaffins from Exxon Chemical Company such as Isopar H and K (C₁₁-C₁₂ isoparaffins), and Isopar L (C₁₁-C₁₃ isoparaffins). Preferred branched hydrocarbons are isohexadecane, isododecane, 2,5-dimethyl decane, isotetradecane, and combinations thereof. Commercially available branched hydrocarbons include Permethyl 99A and 101A (available from Preperse, Inc., South Plainfield, NJ, USA).

Other suitable carriers include isopropanol, butyl alcohol, amyl alcohol, phenyl ethanol, benzyl alcohol, phenyl propanol, ethyl butyrate, isopropyl butyrate, diethyl phthalate, diethyl malonate, diethyl succinate, dimethyl malonate, dimethyl succinate, phenyl ethyl dimethyl carbinol, ethyl-6-acetoxylhexanoate, and methyl (2-pentanyl-3-oxy)cyclopentylacetate, and mixtures thereof. Preferred among such other suitable solvents are diethyl phthalate, diethyl malonate, diethyl succinate, dimethyl malonate, dimethyl succinate, phenylethyl dimethyl carbinol, ethyl-6-acetoxylhexanoate, and mixtures thereof.

Suitable ether carriers are the di(C₅-C₇) alkyl ethers and diethers, especially the di(C₅-C₆) alkyl ethers such as isoamyl ether, dipentyl ether and dihexyl ether.

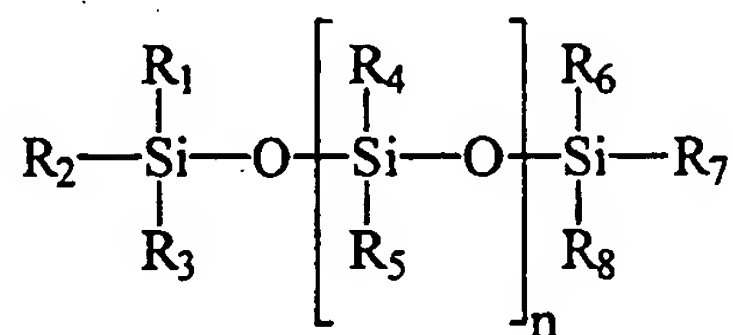
Other suitable carriers for use in the shampoo composition the volatile silicon derivatives such as cyclic or linear polydialkylsiloxane, linear siloxy compounds or silane. The number of silicon atoms in the cyclic silicones is preferably from about 3 to about 7, more preferably about 3 to about 5.

The general formula for such silicones is:



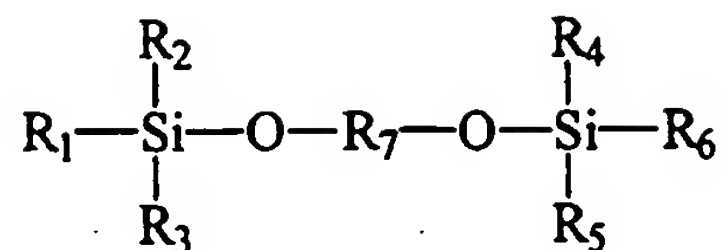
wherein R₁ and R₂ are independently selected from C₁ to C₈ alkyl, aryl or alkylaryl and wherein n=3-7.

The linear polyorgano siloxanes have from about 2 to 7 silicon atoms and have the general formula:



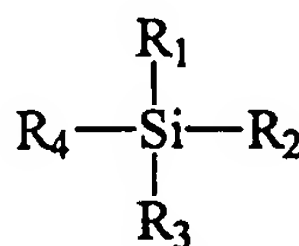
wherein R₁, R₂, R₃, R₄, R₅, R₆, R₇ and R₈ can independently be saturated or unsaturated C₁ - C₈ alkyl, aryl, alkylaryl, hydroxyalkyl, amino alkyl or alkyl siloxy.

Linear siloxy compounds have the general formula:



wherein R₁, R₂, R₃, R₄, R₅, and R₆ are independently selected from saturated or unsaturated C₁ to C₇ alkyl, aryl and alkyl aryl and R₇ is C₁ to C₄ alkylene.

Silane compounds have the general formula:



wherein R₁, R₂, R₃, and R₄ can independently be selected from C₁ - C₈ alkyl, aryl, alkylaryl, hydroxyalkyl and alkylsiloxyl.

Silicones of the above type, both cyclic and linear, are offered by Dow Corning Corporation, Dow Corning 344, 345 and 200 fluids, Union Carbide, Silicone 7202 and Silicone 7158, and Stauffer Chemical, SWS-03314.

The linear volatile silicones generally have viscosities of less than about 5 centistokes at 25°C while the cyclic materials have viscosities less than about 10 centistokes. Examples of volatile silicones are described in Todd and Byers, "Volatile Silicone Fluids for Cosmetics", Cosmetics and Toiletries, Vol. 91, January, 1976, pp. 27-32, and also in Silicon Compounds, pages 253-295, distributed by Petrarch Chemicals, which descriptions are incorporated herein by reference.

b) Cationic Deposition Polymer

The shampoo compositions of the present invention may further comprise an organic cationic polymer as a deposition aid for the styling polymer component described hereinafter. The concentration of the cationic polymer in the shampoo composition ranges from about 0.025% to about 3%, preferably from about 0.05% to about 0.5%, more preferably from about 0.1% to about 0.25%, by weight of the shampoo composition.

The cationic polymer for use in the shampoo composition of the present invention contains cationic nitrogen-containing moieties such as quaternary ammonium or cationic protonated amino moieties. The cationic protonated amines can be primary, secondary, or tertiary amines (preferably secondary or tertiary), depending upon the particular species and the selected pH of the styling shampoo composition. The average molecular weight of the cationic polymer is between about 10 million and about 5,000, preferably at least about 100,000, more preferably at least about 200,000, but preferably not more than

about 2 million, more preferably not more than about 1.5 million. The polymers also have a cationic charge density ranging from about 0.2 meq/gm to about 7 meq/gm, preferably at least about 0.4 meq/gm, more preferably at least about 0.6 meq/gm, but also preferably less than about 5 meq/gm, more preferably less than about 2 meq/gm, at the pH of intended use of the shampoo composition, which pH will generally range from about pH 3 to about pH 9, preferably between about pH 4 and about pH 7.

Any anionic counterions can be used in association with the cationic polymers so long as the polymers remain soluble in water, in the shampoo composition, or in a coacervate phase of the shampoo composition, and so long as the counterions are physically and chemically compatible with the essential components of the shampoo composition or do not otherwise unduly impair product performance, stability or aesthetics. Non limiting examples of such counterions include halides (e.g., chlorine, fluorine, bromine, iodine), sulfate and methylsulfate.

The cationic nitrogen-containing moiety of the cationic polymer is generally present as a substituent on all, or more typically on some, of the monomer units thereof. Thus, the cationic polymer for use in the shampoo composition includes homopolymers, copolymers, terpolymers, and so forth, of quaternary ammonium or cationic amine-substituted monomer units, optionally in combination with non-cationic monomers referred to herein as spacer monomers. Non limiting examples of such polymers are described in the *CTFA Cosmetic Ingredient Dictionary*, 3rd edition, edited by Estrin, Crosley, and Haynes, (The Cosmetic, Toiletry, and Fragrance Association, Inc., Washington, D.C. (1982)), which description is incorporated herein by reference.

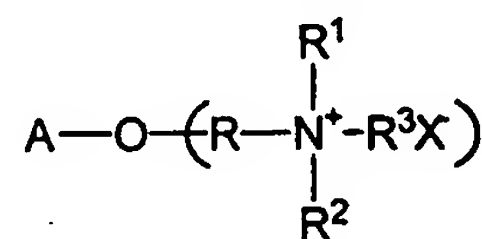
Non limiting examples of suitable cationic polymers include copolymers of vinyl monomers having cationic protonated amine or quaternary ammonium functionalities with water soluble spacer monomers such as acrylamide, methacrylamide, alkyl and dialkyl acrylamides, alkyl and dialkyl methacrylamides, alkyl acrylate, alkyl methacrylate, vinyl caprolactone or vinyl pyrrolidone. The alkyl and dialkyl substituted monomers preferably have from C₁ to C₇ alkyl groups, more preferably from C₁ to C₃ alkyl groups. Other suitable spacer monomers include vinyl esters, vinyl alcohol (made by hydrolysis of polyvinyl acetate), maleic anhydride, propylene glycol, and ethylene glycol.

Suitable cationic protonated amino and quaternary ammonium monomers, for inclusion in the cationic polymers of the shampoo composition herein, include vinyl compounds substituted with dialkyl-aminoalkyl acrylate, dialkylaminoalkyl methacrylate, monoalkylaminoalkyl acrylate, monoalkylaminoalkyl methacrylate, trialkyl methacryloxyalkyl ammonium salt, trialkyl acryloxyalkyl ammonium salt, diallyl quaternary ammonium salts, and vinyl quaternary ammonium monomers having cyclic cationic nitrogen-containing rings such as pyridinium, imidazolium, and quaternized pyrrolidone, e.g., alkyl vinyl imidazolium, alkyl vinyl pyridinium, alkyl vinyl pyrrolidone salts. The alkyl portions of these monomers are preferably lower alkyls such as the C₁, C₂ or C₃ alkyls.

Suitable amine-substituted vinyl monomers for use herein include dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, dialkylaminoalkyl acrylamide, and dialkylaminoalkyl methacrylamide, wherein the alkyl groups are preferably C₁-C₇ hydrocarbyls, more preferably C₁-C₃, alkyls.

Other suitable cationic polymers for use in the shampoo composition include copolymers of 1-vinyl-2-pyrrolidone and 1-vinyl-3-methylimidazolium salt (e.g., chloride salt) (referred to in the industry by the Cosmetic, Toiletry, and Fragrance Association, "CTFA", as Polyquaternium-16), such as those commercially available from BASF Wyandotte Corp. (Parsippany, New Jersey, U.S.A.) under the LUVIQUAT tradename (e.g., LUVIQUAT FC 370); copolymers of 1-vinyl-2-pyrrolidone and dimethylaminoethyl methacrylate (referred to in the industry by CTFA as Polyquaternium-11) such as those commercially available from ISP Corporation (Wayne, New Jersey, U.S.A.) under the GAFQUAT tradename (e.g., GAFQUAT 755N); cationic diallyl quaternary ammonium-containing polymers, including, for example, dimethyldiallylammonium chloride homopolymer and copolymers of acrylamide and dimethyldiallylammonium chloride, referred to in the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively; and mineral acid salts of amino-alkyl esters of homopolymers and copolymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms, as described in U.S. Patent 4,009,256, which description is incorporated herein by reference.

Other suitable cationic polymers for use in the shampoo composition include polysaccharide polymers, such as cationic cellulose derivatives and cationic starch derivatives. Suitable cationic polysaccharide polymers include those which conform to the formula



wherein A is an anhydroglucose residual group, such as a starch or cellulose anhydroglucose residual; R is an alkylene oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof; R₁, R₂, and R₃ independently are alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms, and the total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in R₁, R₂ and R₃) preferably being about 20 or less; and X is an anionic counterion as described in hereinbefore.

Preferred cationic cellulose polymers are those polymers available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR and LR series of polymers, as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10. Another type of preferred cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp. (Edison, NJ, USA) under the trade name Polymer LM-200.

Other suitable cationic polymers include cationic guar gum derivatives, such as guar hydroxypropyltrimonium chloride, specific examples of which include the Jaguar series commercially available from Rhone-Poulenc Incorporated. Other suitable cationic polymers include quaternary nitrogen-containing cellulose ethers, some examples of which are described in U.S. Patent 3,962,418, which description is incorporated herein by reference herein. Other suitable cationic polymers include copolymers of etherified cellulose, guar and starch, some examples of which are described in U.S. Patent 3,958,581, which description is incorporated herein by reference.

The cationic polymers herein are either soluble in the shampoo composition, or preferably are soluble in a complex coacervate phase in the shampoo composition formed by the cationic polymer and the anionic detergent surfactant component described hereinbefore. Complex coacervates of the cationic polymer can also be formed with other charged materials in the shampoo composition.

Coacervate formation is dependent upon a variety of criteria such as molecular weight, component concentration, and ratio of interacting ionic components, ionic strength (including modification of ionic strength, for example, by addition of salts), charge density of the cationic and anionic components, pH, and temperature. Coacervate systems and the effect of these parameters have been described, for example, by J. Caelles, et al., "Anionic and Cationic Compounds in Mixed Systems", *Cosmetics & Toiletries*, Vol. 106, April 1991, pp 49-54, C. J. van Oss, "Coacervation, Complex-Coacervation and Flocculation", *J. Dispersion Science and Technology*, Vol. 9 (5,6), 1988-89, pp 561-573, and D. J. Burgess, "Practical Analysis of Complex Coacervate Systems", *J. of Colloid and Interface Science*, Vol. 140, No. 1, November 1990, pp 227-238, which descriptions are incorporated herein by reference.

It is believed to be particularly advantageous for the cationic polymer to be present in the shampoo composition in a coacervate phase, or to form a coacervate phase upon application or rinsing of the shampoo to or from the hair. Complex coacervates are believed to more readily deposit on the hair. Thus, in general, it is preferred that the cationic polymer exist in the shampoo composition as a coacervate phase or form a coacervate phase upon dilution. If not already a coacervate in the shampoo composition, the cationic polymer will preferably exist in a complex coacervate form in the shampoo upon dilution with water.

Techniques for analysis of formation of complex coacervates are known in the art. For example, microscopic analyses of the shampoo compositions, at any chosen stage of dilution, can be utilized to identify whether a coacervate phase has formed. Such coacervate phase will be identifiable as an additional emulsified phase in the composition. The use of dyes can aid in distinguishing the coacervate phase from other insoluble phases dispersed in the shampoo composition.

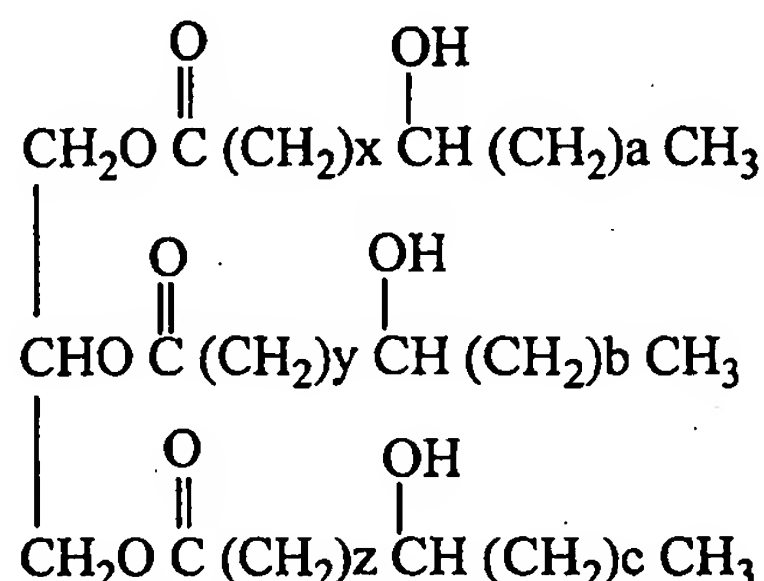
c) Select Stability Active

The shampoo compositions of the present invention may further comprise a select crystalline, hydroxyl-containing stabilizer. The stabilizer is used to form a crystalline stabilizing network in the emulsion that prevents the styling polymer/volatile carrier droplets from coalescing and the shampoo from

phase splitting. Additionally, significantly lower levels of the crystalline, hydroxyl-containing stabilizer need to be used relative to traditional stability actives. This results in enhanced deposition efficiency of the hair styling polymer onto the hair as well as reduced interactions with other shampoo components.

The stabilizers used herein are not surfactants. The stabilizers provide improved shelf and stress stability, but allow the styling polymer/volatile carrier emulsion to separate upon lathering, and thereby provide for increased styling polymer deposition onto the hair.

The stabilizer suitable for use in the shampoo compositions are characterized by the general formula:



wherein: $(x + a)$ is from between 11 and 17,

$(y + b)$ is from between 11 and 17,

(z + c) is from between 11 and 17;

preferably: $x=y=z=10$, and

$$a=b=c=5.$$

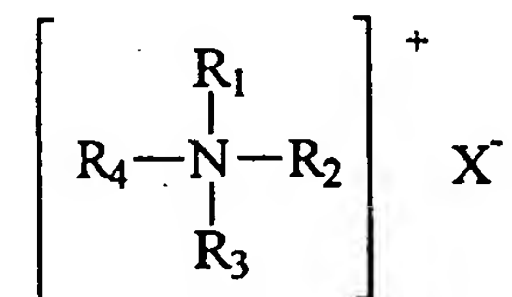
The crystalline, hydroxyl-containing stabilizer comprises from about 0.005% to about 2.0%, preferably from about 0.05% to about 0.25% by weight of the composition. The preferred suspending agent for use in the compositions herein is trihydroxystearin available from Rheox, Inc. (New Jersey, USA) under the tradename Thixcin R.

d) Cationic Spreading Agent

The shampoo compositions of the present invention may further comprise select cationic materials which act as spreading agents. The spreading agents for use in the composition are select quaternary ammonium or protonated amino compounds defined in greater detail hereinafter. These select spreading agents are useful to enhance the morphology of the styling polymer deposit on the hair so that more efficient adhesion between hair fibers results in improved styling performance. The concentration of the select spreading agents in the composition range from about 0.05% to about 5%, preferably from about 0.1% to about 2%, more preferably from about 0.5% to about 1.5%, by weight of the shampoo composition.

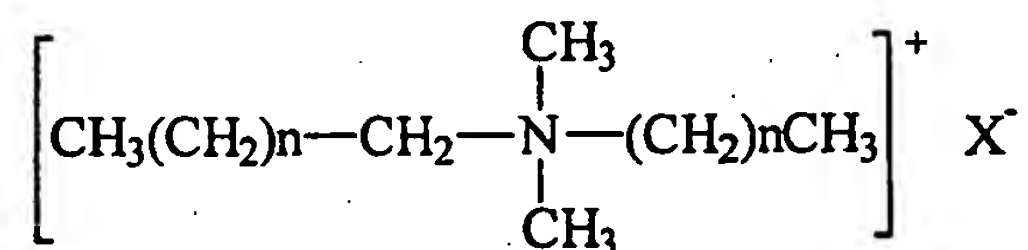
The select spreading agents are quaternary ammonium or amino compounds having 2, 3 or 4 N-radicals which are substituted or unsubstituted hydrocarbon chains having from about 12 to about 30 carbon atoms, wherein the substituents includes nonionic hydrophilic moieties selected from alkoxy, polyoxalkylene, alkylamido, hydroxyalkyl, alkylester moieties, and mixtures thereof. Suitable hydrophile-containing radicals include, for example, compounds having nonionic hydrophile moieties selected from the group consisting of ethoxy, propoxy, polyoxyethylene, polyoxypropylene, ethylamido, propylamido, hydroxymethyl, hydroxyethyl, hydroxypropyl, methylester, ethylester, propylester, or mixtures thereof. The select spreading agents are cationic and must be positively charged at the pH of the shampoo compositions. Generally, the pH of the shampoo composition will be less than about 10, typically from about 3 to about 9, preferably from about 4 to about 8.

Select cationic spreading agents for use in the composition include those corresponding to the formula:



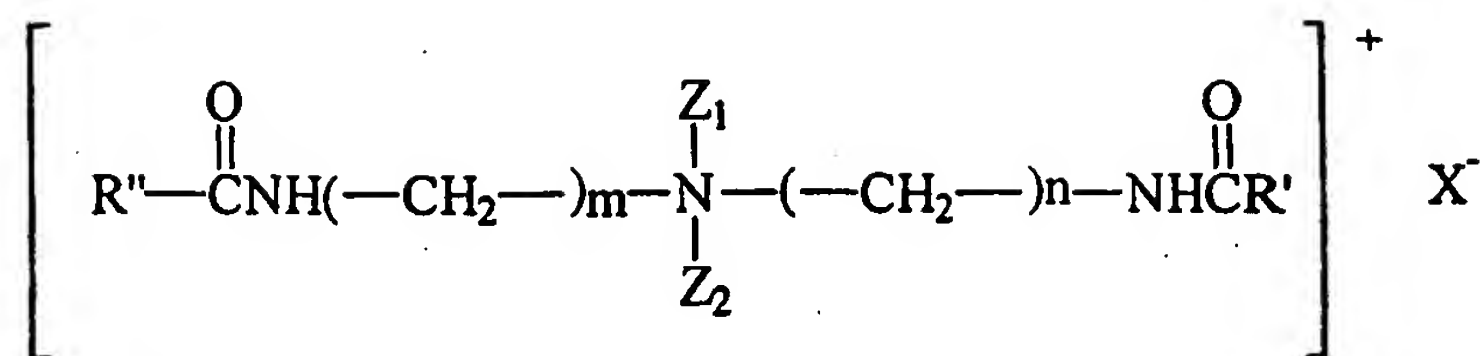
wherein R_1 , and R_2 are independently a saturated or unsaturated, substituted or unsubstituted, linear or branched hydrocarbon chain having from about 12 to about 30 carbon atoms, preferably from about 18 to about 22 carbon atoms, and wherein the hydrocarbon chain can contain one or more hydrophilic moieties selected from the alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, alkylester, and mixtures thereof; R_3 and R_4 are independently a hydrogen, or a saturated or unsaturated, substituted or unsubstituted, linear or branched hydrocarbon chain having from about 1 to about 30 carbon atoms, or a hydrocarbon having from about 1 to about 30 carbon atoms containing one or more aromatic, ester, ether, amido, amino moieties present as substituents or as linkages in the chain, and wherein the hydrocarbon chain can contain one or more hydrophilic moieties selected from the alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, alkylester, and mixtures thereof; and X is a soluble salt forming anion preferably selected from halogen (especially chlorine), acetate, phosphate, nitrate, sulfonate, and alkylsulfate radicals.

An example of a select spreading agent for use in the composition include those corresponding to the formula:



wherein n is from 10-28, preferably 16, and X is a water soluble salt forming anion (e.g., Cl, sulfate, etc.).

Other examples of select cationic spreading agents for use in the composition include those corresponding to the formula:



wherein Z_1 and Z_2 are independently saturated or unsaturated, substituted or unsubstituted, linear or branched hydrocarbons, and preferably Z_1 is an alkyl, more preferably methyl, and Z_2 is a short chain hydroxyalkyl, preferably hydroxymethyl or hydroxyethyl; n and m are independently integers from 1 to 4, inclusive, preferably from 2 to 3, inclusive, more preferably 2; R' and R'' are independently substituted or unsubstituted hydrocarbons, preferably C_{12} - C_{20} alkyl or alkenyl; and X is a soluble salt forming anion (e.g., Cl, sulfate, etc.).

Nonlimiting examples of suitable cationic spreading agents include ditallowdimethyl ammonium chloride, ditallowdimethyl ammonium methyl sulfate, dihexadecyl dimethyl ammonium chloride, di-(hydrogenated tallow) dimethyl ammonium chloride, dioctadecyl dimethyl ammonium chloride, dieicosyl dimethyl ammonium chloride, didocosyl dimethyl ammonium chloride, di-(hydrogenated tallow) dimethyl ammonium acetate, dihexadecyl dimethyl ammonium acetate, ditallow dipropyl ammonium phosphate, ditallow dimethyl ammonium nitrate, di-(coconutalkyl) dimethyl ammonium chloride, ditallowamidoethyl hydroxypropylmonium methosulfate (commercially available as Varisoft 238), dihydrogenated tallowamidoethyl hydroxyethylmonium methosulfate (commercially available as Varisoft 110), ditallowamidoethyl hydroxyethylmonium methosulfate (commercially available as Varisoft 222), and di(partially hardened soyoylethyl) hydroxyethylmonium methosulfate (commercially available as Armocare EQ-S). Ditallowdimethyl ammonium chloride, ditallowamidoethyl hydroxypropylmonium methosulfate, dihydrogenated tallowamidoethyl hydroxyethylmonium methosulfate, ditallowamidoethyl hydroxyethylmonium methosulfate, and di(partially hardened soyoylethyl) hydroxyethylmonium methosulfate are particularly preferred quaternary ammonium cationic surfactants useful herein.

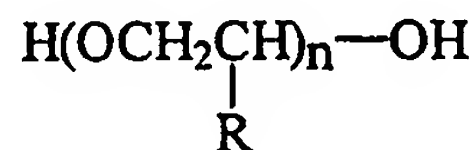
Other suitable quaternary ammonium cationic surfactants are described in M.C. Publishing Co., *McCutcheon's Detergents & Emulsifiers*, (North American edition 1979); Schwartz, et al., *Surface Active Agents. Their Chemistry and Technology*, New York: Interscience Publishers, 1949; U.S. Patent 3,155,591, to Hilfer, issued Nov. 3, 1964; U.S. Patent 3,929,678 to Laughlin et al., issued December 30, 1975; U.S. Patent 3,959,461 to Bailey et al, issued May 25, 1976; and U.S. Patent 4,387,090 to Bolich Jr., issued June 7, 1983, which descriptions are incorporated herein by reference.

e) Polyalkylene Glycol

The shampoo compositions of the present invention may further comprise selected polyalkylene glycols in amounts effective to enhance the conditioned feel of the hair, to mitigate the coated hair feel resulting from the cationic deposition polymer, and to enhance the styling performance of the shampoo. Effective concentrations of the selected polyethylene glycols range from about 0.025% to about 1.5%,

preferably from about 0.05% to about 1.0%, more preferably from about 0.1% to about 0.5%, by weight of the shampoo composition.

The polyalkylene glycols suitable for use in the shampoo compositions are characterized by the general formula:



wherein R is hydrogen, methyl or mixtures thereof, preferably hydrogen, and n is an integer having an average value of from about 1,500 to about 25,000, preferably from about 2,500 to about 20,000, and more preferably from about 3,500 to about 15,000. When R is hydrogen, these materials are polymers of ethylene oxide, which are also known as polyethylene oxides, polyoxyethylenes, and polyethylene glycols. When R is methyl, these materials are polymers of propylene oxide, which are also known as polypropylene oxides, polyoxypropylenes, and polypropylene glycols. When R is methyl, it is also understood that various positional isomers of the resulting polymers can exist.

Specific examples of suitable polyethylene glycol polymers include PEG-14 M wherein R is hydrogen and n has an average value of about 14,000 (PEG-14 M is also known as Polyox WSR® N-3000 available from Union Carbide) and PEG-23 M wherein R is hydrogen and n has an average value of about 23,000 (PEG-23 M is also known as Polyox WSR® N-12K available from Union Carbide).

Suitable polyalkylene polymers include polypropylene glycols and mixed polyethylene/polypropylene glycols.

It has been found that these polyalkylene glycols, when added to the styling shampoo compositions described herein, enhance the conditioned hair feel by mitigating the coated hair feel resulting from deposition of the cationic deposition polymer. Moreover, these polyalkylene glycols also significantly enhance the styling performance versus compositions formulated without polyethylene glycols. This performance is especially surprising as polyalkylene glycols are not known to deliver any styling performance to hair and a synergistic relationship with the other styling shampoo components could not be anticipated.

f) Silicone Hair Conditioning Agent

The shampoo compositions of the present invention may further comprise an optional silicone hair conditioning agent at concentrations effective to provide hair conditioning benefits. Such concentrations range from about 0.01% to about 10%, preferably from about 0.1% to about 8%, more preferably from about 0.1% to about 5%, most preferably from about 0.2% to about 3%, by weight of the shampoo compositions.

The optional silicone hair conditioning agents are insoluble in the shampoo compositions, and are preferably nonvolatile. Typically it will be intermixed in the shampoo composition so as to be in the form of a separate, discontinuous phase of dispersed, insoluble particles, also referred to as droplets. The optional silicone hair conditioning agent phase will comprise a silicone fluid hair conditioning agent such

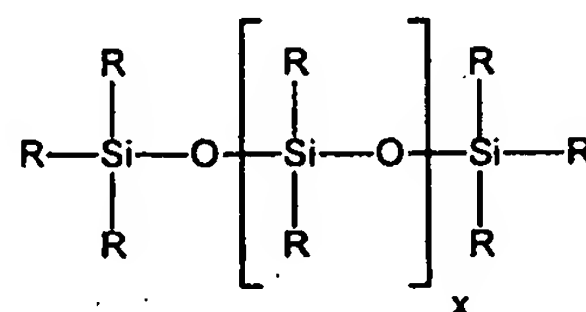
as a silicone fluid and can also comprise other ingredients, such as a silicone resin to improve silicone fluid deposition efficiency or enhance glossiness of the hair (especially when high refractive index (e.g. above about 1.46) silicone conditioning agents are used (e.g. highly phenylated silicones).

The optional silicone hair conditioning agent phase may comprise volatile silicone, nonvolatile silicone, or combinations thereof. Typically, if volatile silicones are present, it will be incidental to their use as a solvent or carrier for commercially available forms of nonvolatile silicone materials ingredients, such as silicone gums and resins.

The optional silicone hair conditioning agents for use in the shampoo compositions preferably have a viscosity of from about 20 to about 2,000,000 centistokes, more preferably from about 1,000 to about 1,800,000 centistokes, even more preferably from about 50,000 to about 1,500,000 centistokes, as measured at 25°C.

Optional silicone fluids include silicone oils which are flowable silicone materials having a viscosity of less than 1,000,000 centistokes, preferably between about 5 and 1,000,000 centistokes, more preferably between about 10 and about 100,000 centistokes, at 25°C. Suitable silicone oils include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers, and combinations thereof. Other insoluble, nonvolatile silicone fluids having hair conditioning properties can also be used.

Optional silicone oils include polyalkyl or polyaryl siloxanes which conform to the following formula (I)



where R is aliphatic, preferably alkyl or alkenyl, or aryl, R can be substituted or unsubstituted, and x is an integer from 1 to about 8,000. Suitable unsubstituted R groups include alkoxy, aryloxy, alkaryl, arylalkyl, arylalkenyl, alkylamine, and ether-substituted, hydroxyl-substituted, and halogen-substituted aliphatic and aryl groups. Suitable R groups also include cationic amines and quaternary ammonium groups.

The aliphatic or aryl groups substituted on the siloxane chain may have any structure so long as the resulting silicones remain fluid at room temperature, are hydrophobic, are neither irritating, toxic nor otherwise harmful when applied to the hair, are compatible with the other components of the shampoo compositions, are chemically stable under normal use and storage conditions, are insoluble in the shampoo compositions herein, and are capable of being deposited on and conditioning the hair.

The two R groups on the silicon atom of each monomeric silicone unit may represent the same or different groups. Preferably, the two R groups represent the same group.

Preferred alkyl and alkenyl substituents are C₁-C₅ alkyls and alkenyls, more preferably from C₁-C₄, most preferably from C₁-C₂. The aliphatic portions of other alkyl-, alkenyl-, or alkynyl-containing

groups (such as alkoxy, alkaryl, and alkamino) can be straight or branched chains and preferably have from one to five carbon atoms, more preferably from one to four carbon atoms, even more preferably from one to three carbon atoms, most preferably from one to two carbon atoms. As discussed above, the R substituents hereof can also contain amino functionalities, e.g. alkamino groups, which can be primary, secondary or tertiary amines or quaternary ammonium. These include mono-, di- and tri- alkylamino and alkoxyamino groups wherein the aliphatic portion chain length is preferably as described above. The R substituents can also be substituted with other groups, such as halogens (e.g. chloride, fluoride, and bromide), halogenated aliphatic or aryl groups, and hydroxy (e.g. hydroxy substituted aliphatic groups). Suitable halogenated R groups could include, for example, tri-halogenated (preferably fluoro) alkyl groups such as $-R^1-C(F)_3$, wherein R^1 is C_1-C_3 alkyl. Examples of such polysiloxanes include polymethyl -3,3,3 trifluoropropylsiloxane.

Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred silicones are polydimethyl siloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane is especially preferred. Other suitable R groups include methyl, methoxy, ethoxy, propoxy, and aryloxy. The three R groups on the end caps of the silicone may also represent the same or different groups.

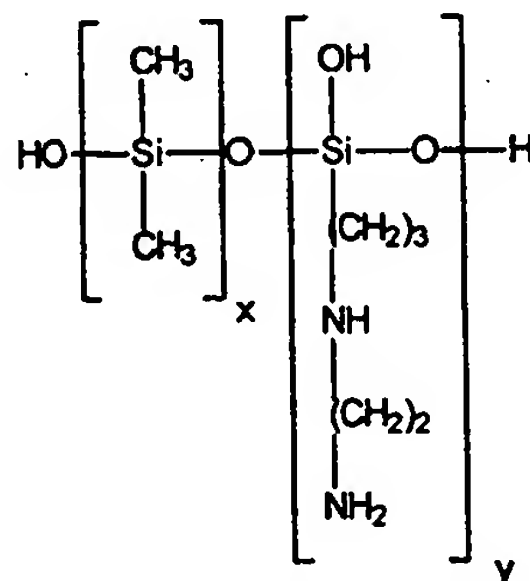
The nonvolatile polyalkylsiloxane fluids that may be used include, for example, polydimethylsiloxanes. These siloxanes are available, for example, from the General Electric Company in their Viscasil R and SF 96 series, and from Dow Corning in their Dow Corning 200 series.

The polyalkylaryl siloxane fluids that may be used, also include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

The polyether siloxane copolymers that may be used include, for example, a polypropylene oxide modified polydimethylsiloxane (e.g., Dow Corning DC-1248) although ethylene oxide or mixtures of ethylene oxide and propylene oxide may also be used. The ethylene oxide and polypropylene oxide concentrations must be sufficiently low to prevent solubility in water and the composition hereof.

Suitable alkylamino substituted silicones include those which conform to the following structure

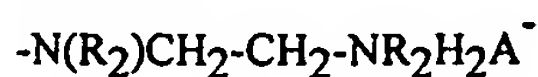
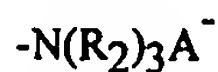
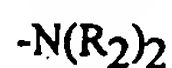
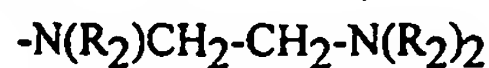
(II)



wherein x and y are integers. This polymer is also known as "amodimethicone".

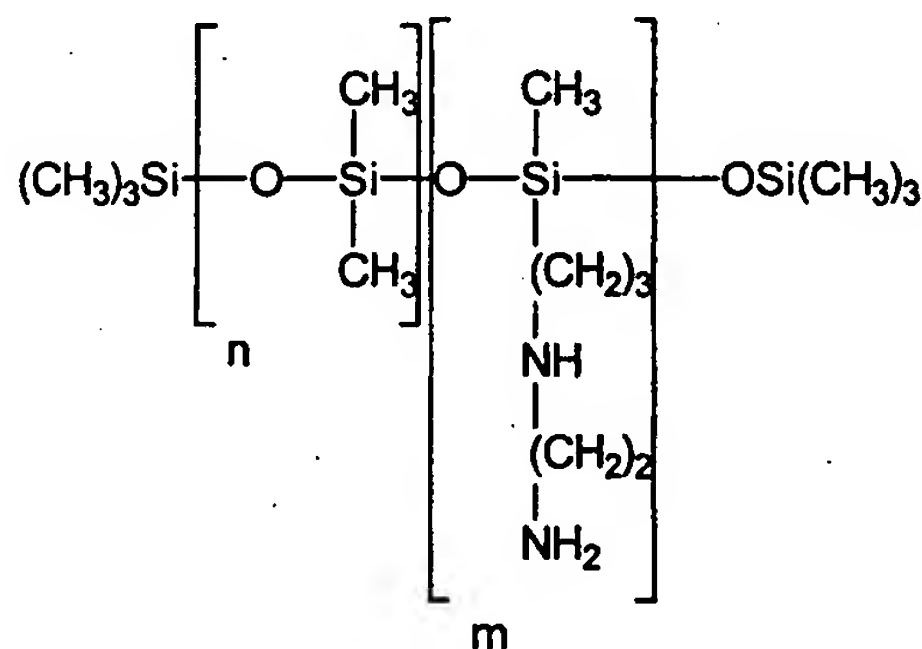
Suitable cationic silicone fluids include those which conform to the formula (III)

$(R_1)_a G_{3-a} - Si - (-OSiG_2)_n - (-OSiG_b(R_1)_{2-b})_m - O - SiG_{3-a}(R_1)_a$, wherein G is selected from the group consisting of hydrogen, phenyl, hydroxy, C_1 - C_8 alkyl and preferably methyl; a is 0 or an integer having a value from 1 to 3, preferably 0; b is 0 or 1, preferably 1; the sum $n+m$ is a number from 1 to 2,000 and preferably from 50 to 150, n being able to denote a number from 0 to 1,999 and preferably from 49 to 149 and m being able to denote an integer from 1 to 2,000 and preferably from 1 to 10; R_1 is a monovalent radical conforming to the formula $C_qH_{2q}L$ in which q is an integer having a value of from 2 to 8 and L is selected from the following groups:

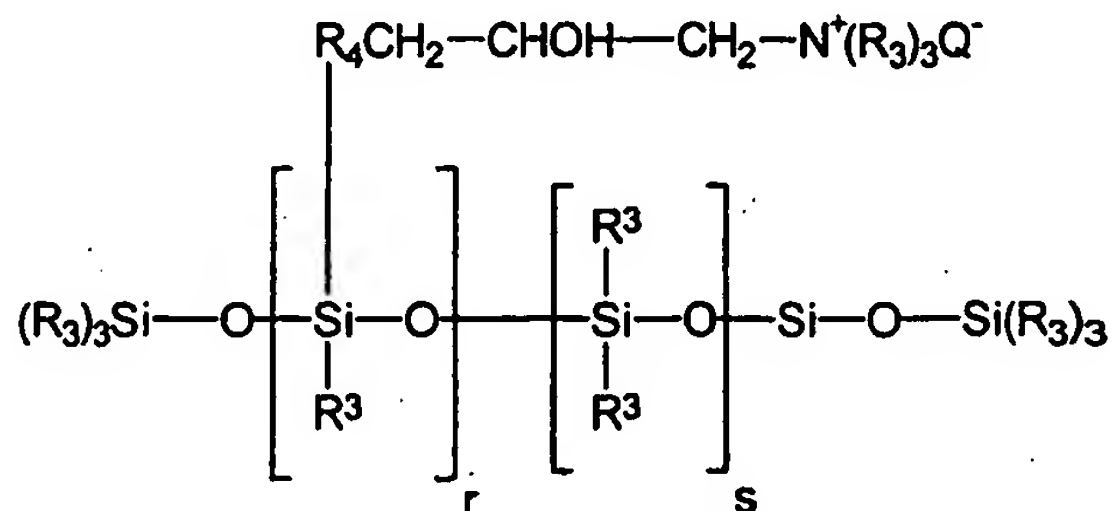


in which R_2 is selected from the group consisting of hydrogen, phenyl, benzyl, a saturated hydrocarbon radical, preferably an alkyl radical containing from 1 to 20 carbon atoms, and A^- is a halide ion.

An especially preferred cationic silicone corresponding to formula (III) is the polymer known as "trimethylsilylamodimethicone", of formula (IV):



Other silicone cationic polymers which can be used in the shampoo compositions are represented by the formula (V):

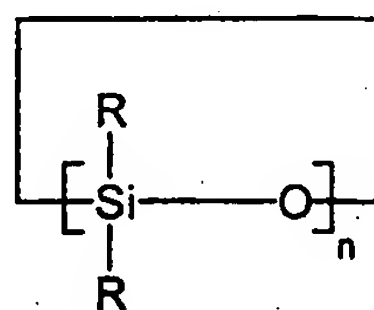


where R^3 denotes a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, preferably an alkyl or alkenyl radical such as methyl; R_4 denotes a hydrocarbon radical, preferably a C_1 - C_{18} alkylene radical or a C_1 - C_{18} , and more preferably C_1 - C_8 , alkyleneoxy radical; Q^- is a halide ion, preferably chloride; r denotes an average statistical value from 2 to 20, preferably from 2 to 8; s denotes an average statistical value from 20 to 200, and preferably from 20 to 50. A preferred polymer of this class is available from Union Carbide under the name "UCAR SILICONE ALE 56."

Other optional silicone fluids are the insoluble silicone gums. These gums are polyorganosiloxane materials having a viscosity at 25°C of greater than or equal to 1,000,000 centistokes. Silicone gums are described in U.S. Patent 4,152,416; Noll and Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968; and in General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76, all of which are incorporated herein by reference. The silicone gums will typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and about 1,000,000, specific examples of which include polydimethylsiloxane, (polydimethylsiloxane) (methylvinylsiloxane) copolymer, poly(dimethylsiloxane) (diphenyl siloxane)(methylvinylsiloxane) copolymer and mixtures thereof.

Another category of nonvolatile, insoluble silicone fluid conditioning agents are the high refractive index silicones, having a refractive index of at least about 1.46, preferably at least about 1.48, more preferably at least about 1.52, most preferably at least about 1.55. The refractive index of the polysiloxane fluid will generally be less than about 1.70, typically less than about 1.60. In this context, polysiloxane "fluid" includes oils as well as gums.

The high refractive index polysiloxane fluid includes those represented by general Formula (I) above, as well as cyclic polysiloxanes such as those represented by Formula (VI) below:



wherein R is as defined above, n is from about 3 to about 7, preferably from 3 to 5.

The high refractive index polysiloxane fluids contain a sufficient amount of aryl-containing R substituents to increase the refractive index to the desired level, which is described above. In addition, R and n must be selected so that the material is nonvolatile, as defined above.

Aryl-containing substituents contain alicyclic and heterocyclic five and six membered aryl rings, and substituents containing fused five or six membered rings. The aryl rings themselves can be substituted or unsubstituted. Substituents include aliphatic substituents, and can also include alkoxy substituents, acyl substituents, ketones, halogens (e.g., Cl and Br), amines, etc. Exemplary aryl-containing groups include substituted and unsubstituted arenes, such as phenyl, and phenyl derivatives such as

phenyls with C_1 - C_5 alkyl or alkenyl substituents, e.g., allylphenyl, methyl phenyl and ethyl phenyl, vinyl phenyls such as styrenyl, and phenyl alkynes (e.g. phenyl C_2 - C_4 alkynes). Heterocyclic aryl groups include substituents derived from furan, imidazole, pyrrole, pyridine, etc. Fused aryl ring substituents include, for example, naphthalene, coumarin, and purine.

In general, the high refractive index polysiloxane fluids will have a degree of aryl-containing substituents of at least about 15%, preferably at least about 20%, more preferably at least about 25%, even more preferably at least about 35%, most preferably at least about 50%. Typically, although it is not intended to necessarily limit the invention, the degree of aryl substitution will be less than about 90%, more generally less than about 85%, preferably from about 55% to about 80%.

The polysiloxane fluids are also characterized by relatively high surface tensions as a result of their aryl substitution. In general, the polysiloxane fluids hereof will have a surface tension of at least about 24 dynes/cm², typically at least about 27 dynes/cm². Surface tension, for purposes hereof, is measured by a de Nouy ring tensiometer according to Dow Corning Corporate Test Method CTM 0461, November 23, 1971. Changes in surface tension can be measured according to the above test method or according to ASTM Method D 1331.

Preferred high refractive index polysiloxane fluids have a combination of phenyl or phenyl derivative substituents (preferably phenyl), with alkyl substituents, preferably C_1 - C_4 alkyl (most preferably methyl), hydroxy, C_1 - C_4 alkylamino (especially $-R^1NHR^2NH_2$ where each R^1 and R^2 independently is a C_1 - C_3 alkyl, alkenyl, and/or alkoxy. High refractive index polysiloxanes are available from Dow Corning Corporation (Midland, Michigan, U.S.A.) Huls America (Piscataway, New Jersey, U.S.A.), and General Electric Silicones (Waterford, New York, U.S.A.).

References disclosing examples of some suitable silicone fluids for use in the shampoo compositions include U.S. Patent 2,826,551, U.S. Patent 3,964,500, U.S. Patent 4,364,837, British Patent 849,433, and Silicon Compounds, Petrarch Systems, Inc. (1984), all of which are incorporated herein by reference.

Silicone resins can be included in the silicone conditioning agent. These resins are highly crosslinked polymeric siloxane systems. The crosslinking is introduced through the incorporation of trifunctional and tetrafunctional silanes with monofunctional or difunctional, or both, silanes during manufacture of the silicone resin. As is well understood in the art, the degree of crosslinking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetrafunctional siloxane monomer units (and hence, a sufficient level of crosslinking) such that they dry down to a rigid, or hard, film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone resins herein. Preferably, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Silanes used in the manufacture of silicone

resins include monomethyl-, dimethyl-, trimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and methylvinyl-chlorosilanes, and tetrachlorosilane, with the methyl-substituted silanes being most commonly utilized. Preferred resins are offered by General Electric as GE SS4230 and SS4267. Commercially available silicone resins will generally be supplied in a dissolved form in a low viscosity volatile or nonvolatile silicone fluid. The silicone resins for use herein should be supplied and incorporated into the present compositions in such dissolved form, as will be readily apparent to those skilled in the art.

Background material on silicones including sections discussing silicone fluids, gums, and resins, as well as manufacture of silicones, can be found in Encyclopedia of Polymer Science and Engineering, Volume 15, Second Edition, pp 204-308, John Wiley & Sons, Inc., 1989, incorporated herein by reference.

Silicone materials and silicone resins in particular, can conveniently be identified according to a shorthand nomenclature system well known to those skilled in the art as "MDTQ" nomenclature. Under this system, the silicone is described according to presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the monofunctional unit $(\text{CH}_3)_3\text{SiO}_{0.5}$; D denotes the difunctional unit $(\text{CH}_3)_2\text{SiO}$; T denotes the trifunctional unit $(\text{CH}_3)\text{SiO}_{1.5}$; and Q denotes the quadri- or tetra-functional unit SiO_2 . Primes of the unit symbols, e.g., M', D', T', and Q' denote substituents other than methyl, and must be specifically defined for each occurrence. Typical alternate substituents include groups such as vinyl, phenyls, amines, hydroxyls, etc. The molar ratios of the various units, either in terms of subscripts to the symbols indicating the total number of each type of unit in the silicone (or an average thereof) or as specifically indicated ratios in combination with molecular weight complete the description of the silicone material under the MDTQ system. Higher relative molar amounts of T, Q, T' and/or Q' to D, D', M and/or M' in a silicone resin is indicative of higher levels of crosslinking. As discussed before, however, the overall level of crosslinking can also be indicated by the oxygen to silicon ratio.

The silicone resins for use herein which are preferred are MQ, MT, MTQ, MDT and MDTQ resins. Thus, the preferred silicone substituent is methyl. Especially preferred are MQ resins wherein the M:Q ratio is from about 0.5:1.0 to about 1.5:1.0 and the average molecular weight of the resin is from about 1000 to about 10,000.

The weight ratio of the nonvolatile silicone fluid, having refractive index below 1.46, to the silicone resin component, when used, is preferably from about 4:1 to about 400:1, preferably this ratio is from about 9:1 to about 200:1, more preferably from about 19:1 to about 100:1, particularly when the silicone fluid component is a polydimethylsiloxane fluid or a mixture of polydimethylsiloxane fluid and polydimethylsiloxane gum as described above. Insofar as the silicone resin forms a part of the same phase in the compositions hereof as the silicone fluid, i.e. the conditioning active, the sum of the fluid and resin should be included in determining the level of silicone conditioning agent in the composition.

g) Optional Agents

The shampoo compositions of the present invention may further comprise additional materials which improve the performance and/or aesthetics of the compositions of the present invention. These materials compete with other shampoo composition materials for solubilization by the surfactant component. As a result, they impact both the amount of coacervate which forms upon dilution and the composition of this coacervate. Additionally, the additional optional agents are also entrapped in the coacervate. The styling polymer/volatile carrier droplets are deposited onto the hair by the coacervate, thus these optional agents can be used to directly influence styling performance by impacting the amount of coacervate formed as well as hair feel by impacting the composition of the coacervate.

Highly preferred optional agents includes crystalline materials that can be categorized as acyl derivatives, long chain amine oxides, or combinations thereof, concentrations of which range from about 0.1% to about 5.0%, preferably from about 0.5% to about 3.0%, by weight of the shampoo compositions. These agents are described as suspending agents in U.S. Patent 4,741,855, and U.S. Reissue Patent 34,584 (Grote et al.), which descriptions are incorporated herein by reference. These preferred materials include ethylene glycol esters of fatty acids preferably having from about 16 to about 22 carbon atoms. More preferred are the ethylene glycol stearates, both mono and distearate, but particularly the distearate containing less than about 7% of the mono stearate. Other suitable optional agents include alkanol amides of fatty acids, preferably having from about 16 to about 22 carbon atoms, more preferably about 16 to 18 carbon atoms, preferred examples of which include stearic monoethanolamide, stearic diethanolamide, stearic monoisopropanolamide and stearic monoethanolamide stearate. Other long chain acyl derivatives include long chain esters of long chain fatty acids (e.g., stearyl stearate, cetyl palmitate, etc.); glyceryl esters (e.g., glyceryl distearate) and long chain esters of long chain alkanol amides (e.g., stearamide diethanolamide distearate, stearamide monoethanolamide stearate). Long chain acyl derivatives, ethylene glycol esters of long chain carboxylic acids, long chain amine oxides, and alkanol amides of long chain carboxylic acids in addition to the preferred materials listed above may be used as suspending agents.

Other long chain acyl derivatives suitable for use as additional optional agents include N,N-dihydrocarbyl amido benzoic acid and soluble salts thereof (e.g., Na, K), particularly N,N-di(hydrogenated) C₁₆, C₁₈ and tallow amido benzoic acid species of this family, which are commercially available from Stepan Company (Northfield, Illinois, USA).

Examples of suitable long chain amine oxides include alkyl (C₁₆-C₂₂) dimethyl amine oxides, e.g., stearyl dimethyl amine oxide.

Method of Use

The shampoo compositions of the present invention are used in a conventional manner for cleansing and styling hair. An effective amount of the composition for cleansing and styling the hair is applied to the hair, that has preferably been wetted with water, and is then rinsed off. Such effective amounts generally range from about 1gm to about 50gm, preferably from about 1gm to about 20gm.

Application to the hair typically includes working the composition through the hair such that most or all of the hair is contacted with the composition.

This method for cleansing and styling the hair comprises the steps of a) wetting the hair with water, b) applying an effective amount of the shampoo composition to the hair, c) shampooing the hair with the composition, and d) rinsing the composition from the hair with water. These steps can be repeated as many times as desired to achieve the cleansing and styling benefit desired. The method is preferably employed daily, every other day, or every third day, to provide and maintain the hair cleansing and styling performance described herein.

Examples

The styling shampoo compositions illustrated in Examples I-X illustrate specific embodiments of the shampoo compositions of the present invention, but are not intended to be limiting thereof. Other modifications can be undertaken by the skilled artisan without departing from the spirit and scope of this invention. These exemplified embodiments of the styling shampoo compositions of the present invention provide cleansing of hair and improved hair styling performance.

The shampoo compositions illustrated in Examples I-X are prepared by conventional formulation and mixing methods, an example of which is set forth hereinbelow. All exemplified amounts are listed as weight percents and exclude minor materials such as diluents, filler, and so forth, unless otherwise specified.

Preparation

The styling shampoo compositions of the present invention may be prepared using conventional formulation and mixing techniques. The hair styling polymer should first be dissolved in the volatile carrier. This styling polymer/volatile carrier premix may then be added to a premix of the surfactants, or some portion of the surfactants, and the solid components which has been heated to melt the solid components, e.g., about 87°C. This mixture is then pumped through a high shear mill and cooled, and then the remaining components are mixed in. Alternatively, the styling polymer/volatile carrier premix may be added to this final mix, after cooling. The composition should have a final viscosity of from about 2000 to about 12,000 cps. The viscosity of the composition can be adjusted using sodium chloride or ammonium xylenesulfonate as needed.

The styling polymer/volatile solvent premix, as exemplified in the following examples, may be a combination of styling polymers/solvent as described hereinbelow.

Mixture A. w/w ratio

Styling Polymer: t-butyl acrylate/2-ethylhexyl methacrylate (90/10 w/w)	40
Volatile Solvent: isododecane	60

Mixture B.

	w/w ratio
Styling Polymer: t-butyl acrylate/2-ethylhexyl methacrylate (90/10 w/w)	50
Volatile Solvent: isododecane	50

Mixture C.

w/w ratio

Styling Polymer: t-butyl acrylate/2-ethylhexyl methacrylate/ PDMS macromer
(81/9/10 w/w; Polymer wt avg. M.W. = 100,000)

Volatile Solvent: isododecane

40

60

Component	Weight %				
	I	II	III	IV	V
Ammonium Laureth Sulfate	9.0	9.0	9.0	9.0	9.0
Ammonium Lauryl Sulfate	3.0	3.0	3.0	3.0	3.0
Lauroamphoacetate	6.0	6.0	6.0	6.0	6.0
Mixture A	---	4.0	4.0	4.0	---
Mixture B	4.0	---	---	---	4.0
Dihydrogenated Tallowamidoethyl Hydroxyethylmonium Methosulfate (1)	---	---	1.0	1.0	---
Ditallowamidoethyl Hydroxypropylmonium Methosulfate (2)	---	---	---	---	1.0
Citric Acid	1.0	0.88	1.0	1.0	1.0
Laureth 4	0.17	0.17	0.17	0.17	0.17
Monosodium Phosphate	---	0.1	---	---	---
Disodium Phosphate	---	0.2	---	---	---
Glycol Distearate	2.0	2.0	2.0	1.43	2.0
Cocomonoethanol amide	0.6	0.6	0.6	0.6	0.6
Fragrance	1.0	1.0	1.0	1.0	1.0
Cetyl Alcohol	---	0.42	0.42	---	0.42
Trihydroxystearin	0.05	0.25	0.15	0.15	0.15
Polyquaternium 10 (JR30M)	0.15	---	---	---	0.15
Guar Hydroxypropyltrimonium Chloride (3)	0.15	0.3	0.3	0.3	0.15
Dimethicone	0.25	0.5	0.25	1.0	0.25
DMDM Hydantoin	0.2	0.2	0.2	0.2	0.2
Water	qs 100	qs 100	qs 100	qs 100	qs 100

(1) Available under the tradename Varisoft 110 from Sherex Chemical Co. (Dublin, Ohio, USA)

(2) Available under the tradename Varisoft 238 from Sherex Chemical Co. (Dublin, Ohio, USA)

(3) Available under the tradename Jaguar C-17 from Rhone-Poulenc. (Cranbury, New Jersey, USA)

Component	Weight %				
	VI	VII	VIII	IX	X
Ammonium Laureth Sulfate	9.0	9.0	9.0	9.0	9.0
Ammonium Lauryl Sulfate	3.0	3.0	3.0	3.0	3.0
Lauroamphoacetate	6.0	6.0	6.0	6.0	6.0
Mixture A	4.0	---	4.0	---	4.0
Mixture B	---	4.0	---	---	---
Mixture C	---	---	---	4.0	---
Dihydrogenated Tallowamidoethyl Hydroxyethylmonium Methosulfate (1)	1.0	0.8	---	1.0	1.0
PEG 14M	0.3	0.15	0.3	---	---
PEG 23M	---	---	---	0.3	0.15
Citric Acid	1.0	1.0	1.0	1.0	1.0
Laureth 4	0.17	0.17	0.17	0.17	0.17
Glycol Distearate	2.0	1.43	2.0	1.43	2.0
Fragrance	1.0	1.0	1.0	1.0	1.0
Cetyl Alcohol	0.42	---	0.42	---	0.42
Trihydroxystearin	0.15	0.05	0.25	0.15	0.15
Polyquaternium 10 (JR30M)	0.15	---	0.15	---	0.1
Guar Hydroxypropyltrimonium Chloride (3)	0.15	0.3	0.15	0.3	0.2
Dimethicone	0.25	0.25	1.0	0.25	---

DMDM Hydantoin
Water

0.2	0.2	0.2	0.2	0.2
qs 100	qs 100	qs 100	qs 100	qs 100

- (1) Available under the tradename Varisoft 110 from Sherex Chemical Co. (Dublin, Ohio, USA)
(3) Available under the tradename Jaguar C-17 from Rhone-Poulenc. (Cranbury, New Jersey, USA)

WHAT IS CLAIMED IS:**1. A styling shampoo composition comprising:**

- (a) from 5% to 50% by weight of a deterative surfactant selected from the group consisting of anionic surfactants, zwitterionic surfactants, and amphoteric surfactants, and combinations thereof;
- (b) from 0.1% to 10% by weight of an organic hair styling polymer wherein the organic hair styling polymer is not a vinyl pyrrolidone/vinyl acetate copolymer; and
- (c) from 40% to 94.9% by weight of water;

wherein the composition is characterized by having a Hair Feel Index (HFI) is greater than or equal to 0.65 and a Curl Retention Value (CRV) is greater than or equal to 70.

2. A styling shampoo composition comprising:

- (a) from 5% to 50% by weight of a deterative surfactant selected from the group consisting of anionic surfactants, zwitterionic surfactants, and amphoteric surfactants, and combinations thereof;
- (b) from 0.1% to 10% by weight of a silicone-grafted hair styling polymer having a weight average molecular weight of greater than 10,000 and less than 300,000; and
- (c) from 40% to 94.9% by weight of water;

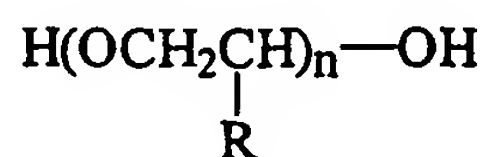
wherein the composition is characterized by having a Hair Feel Index (HFI) is greater than or equal to 0.65 and a Curl Retention Value (CRV) is greater than or equal to 70.

3. A styling shampoo composition comprising:

- (a) from 5% to 50% by weight of a deterative surfactant selected from the group consisting of anionic surfactants, zwitterionic and amphoteric surfactants, and combinations thereof;
- (b) from 0.025% to 3% by weight of an organic cationic deposition polymer which has a cationic charge density of from 0.2 meq/gm to 7 meq/gm and an average molecular weight of from 5,000 to 10 million;
- (c) from 0.1% to 10% by weight of a water-insoluble hair styling polymer;
- (d) from 0.1% to 10% by weight of a volatile, water-insoluble carrier for the hair styling polymer;
- (e) from 0.005% to 2.0% by weight of a crystalline hydroxyl-containing stabilizing agent; and
- (f) from 22% to 94.3% by weight water;

wherein the composition is characterized by having a Hair Feel Index (HFI) is greater than or equal to 0.65 and a Curl Retention Value (CRV) is greater than or equal to 70.

4. The composition according to any of the preceding claims wherein the anionic surfactant is selected from the group consisting of ammonium lauryl sulfate, ammonium laureth sulfate, alkyl glyceryl ether sulfonate, and mixtures thereof; the amphoteric surfactant is selected from the group consisting of lauroamphoacetate, lauroamphodiacetate, cocoamphoacetate, cocoamphodiacetate, and mixture thereof; and the zwitterionic surfactant is a betaine surfactant.
5. The composition according to any of the preceding claims wherein the composition comprises from 0.1% to 0.25% by weight of the organic cationic deposition polymer having a cationic charge density of from 0.6 meq/g to 2.0 meq/g.
6. The composition according to any of the preceding claims wherein the organic cationic deposition polymer is selected from the group consisting of cationic cellulose derivatives, cationic starch derivatives, cationic guar gum derivatives, and combinations thereof.
7. The composition according to any of the preceding claims wherein the water-insoluble hair styling polymer is an organic styling polymer selected from the group consisting of *t*-butyl acrylate/2-ethylhexyl acrylate copolymers having a weight/weight ratio of monomers of 95/5, 90/10, 80/20, 70/30, 60/40, and 50/50; *t*-butyl acrylate/2-ethylhexyl methacrylate copolymers having a weight/weight ratio of monomers of 95/5, 90/10, 80/20, 70/30, 60/40, and 50/50; *t*-butyl methacrylate/2-ethylhexyl acrylate copolymers having a weight/weight ratio of monomers of 95/5, 90/10, 80/20, 70/30, 60/40, and 50/50; *t*-butyl methacrylate/2-ethylhexyl methacrylate copolymers having a weight/weight ratio of monomers of 95/5, 90/10, 80/20, 70/30, 60/40, and 50/50; vinyl pyrrolidone/vinyl acetate copolymers having a weight/weight ratio of monomers of 10/90, and 5/95; and mixtures thereof.
8. The composition according to any of the preceding claims which further comprises from 0.05% to 5% by weight of a non-polymeric, cationic spreading agent, that comprises from two to four N-radicals, wherein the N-radicals are substituted or unsubstituted carbon chains having from 12 to 30 carbon atoms.
9. The composition according to any of the preceding claims which further comprises from 0.025% to 1.5% of a polyalkylene glycol, wherein said polyalkylene glycol is characterized by the general formula:



wherein R is hydrogen, methyl or mixtures thereof, and n is an integer having an average value of from 1,500 to 25,000.

10. The composition according to any of the preceding claims wherein the crystalline hydroxyl-containing stabilizing agent is trihydroxystearin.
11. The composition according to any of the preceding claims wherein the water-insoluble hair styling polymer is a silicone grafted polymer selected from the group consisting of:
 - (i) t-butylacrylate/t-butyl-methacrylate/2-ethylhexyl-methacrylate/PDMS macromer-20,000 molecular weight macromer 31/27/32/10;
 - (ii) t-butylmethacrylate/2-ethylhexyl-methacrylate/PDMS macromer-15,000 molecular weight macromer 75/10/15;
 - (iii) t-butylmethacrylate/2-ethylhexyl-acrylate/PDMS macromer-10,000 molecular weight macromer 65/15/20;
 - (iv) t-butylacrylate/2-ethylhexyl-acrylate/PDMS macromer-14,000 molecular weight macromer 77/11/12;
 - (v) t-butylacrylate/2-ethylhexyl-methacrylate/PDMS macromer-13,000 molecular weight macromer 81/9/10; and
 - (vi) and mixtures thereof.
12. The composition according to any of the preceding claims wherein the water-insoluble volatile solvent is selected from the group consisting of dodecane, isododecane, isotetradecane, isohexadecane, 2,5-dimethyldecane, diethyl succinate, dimethyl succinate, diethyl malonate, dimethyl malonate, cyclomethicone, and mixtures thereof.
13. The composition according to any of the preceding claims wherein the composition comprises a weight ratio of the water-insoluble hair styling polymer to the water-insoluble solvent of from 30:70 to 60:40.
14. The composition according to any of the preceding claims wherein the composition further comprises a non-volatile silicone conditioning agent selected from the group consisting of polyarylsiloxanes, polyalkyl siloxanes, polyalkylarylsiloxanes, derivatives thereof, and mixtures thereof.
15. The composition according to any of the preceding claims which further comprises from about 0.1% to about 5% of an ethylene glycol stearate.

INTERNATIONAL SEARCH REPORT

In tional Application No
PCT/US 99/02311

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 38673 A (STEPAN) 23 October 1997 see claims 1,13,23 see page 21, line 11-21 see page 23, line 28 - page 24, line 25 see tables 3,4 ----	1,4,9,14
A	FR 2 740 037 A (RHONE POULENC CHIMIE) 25 April 1997 see claims 1,9 see page 8, line 25 - page 9, line 16 see page 10, line 1-24 see page 12, line 15-26 see page 13, line 8-26 ----- -/--	1-4,6, 9-11

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

28 June 1999

Date of mailing of the international search report

13/07/1999

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/02311

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 412 704 A (PROCTER & GAMBLE)</p> <p>13 February 1991</p> <p>see claim 1</p> <p>see page 9, line 21 - page 10, line 55</p> <p>see page 12, line 58 - page 13, line 48</p> <p>-----</p>	1,2,4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 99/ 02311

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
Claims 1,2 and 3 are dealing with physical parameters. As a search on physical parameters is not possible, the search has been performed according to the wording of the claims 1, 2 and 3.

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/02311

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9738673	A	23-10-1997	AU 6969196 A EP 0904052 A	07-11-1997 31-03-1999
FR 2740037	A	25-04-1997	NONE	
EP 412704	A	13-02-1991	AT 179323 T AU 624014 B AU 6015890 A CA 2022467 A,C CN 1049784 A DE 69033073 D EP 0878184 A JP 3128311 A MX 173186 B TR 25185 A US 5618524 A US 5658557 A	15-05-1999 28-05-1992 07-02-1991 08-02-1991 13-03-1991 02-06-1999 18-11-1998 31-05-1991 07-02-1994 01-11-1992 08-04-1997 19-08-1997